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Experimental Evaluation of Fuel Oil Additives for Reducing Emissions and Increasing Efficiency of Boilers

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16. ABSTRACT The report gives results of an evaluation of the effectiveness of combustion-type fuel oil additives to reduce emissions and increase efficiency in a 50-bhp (500 kw) commercial oil-fired packaged boiler. Most additive evaluation runs were made during continuous firing, constant-load operation of the boiler. Additives, both proprietary and pure compounds, containing alkaline-earth and transition metals in concentrations between 20 and 50 ppm were effective in reducing carbon particulate emissions by as much as 100 percent when firing residual oil. They also were effective in reducing emissions of smoke and polycyclic organic matter. No additive was found to be effective in reducing either NOx or SOx. Certain of these additives used in residual oil permitted an increase in overall boiler efficiency by reducing stack gas loss, without increasing particulate emissions. This efficiency gain, about 2%, was achieved by: appropriate readjustment to permit boiler operation at lower excess air levels; and reducing the fouling of boiler heat-transfer surfaces. Both proprietary and pure compounds were found to be equally effective. Thus, if additives are used, cost savings can be maximized by using the less expensive pure compounds.

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EXPERIMENTAL EVALUATION OF FUEL OIL ADDITIVES FOR REDUCING EMISSIONS AND INCREASING EFFICIENCY OF BOILERS

by

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ABSTRACT

In this research program, the effectiveness of combustion-type fuel-oil additives to reduce emissions and increase efficiency was evaluated in a 50-bhp (500 kW) commercial oil-fired packaged boiler. Most additive evaluation runs were made during continuous firing, constant-load operation of the boiler.

Additives, both proprietary and pure compounds, containing certain alkaline-earth and transition metals in concentration in the range of 20 ppm to 50 ppm were effective in reducing carbon particulate emissions by as much as 100 percent when firing residual oil. These additives also were effective in reducing emissions of smoke and polycyclic organic matter. No additive was found to be effective in reducing either nitrogen oxides or sulfur oxides.

Certain of these additives used in residual oil permitted an increase in overall boiler efficiency by reducing stack gas loss, without increasing particulate emissions. This efficiency gain, approximately 2 percent, was achieved through (1) appropriate readjustment to permit boiler operation at lower excess air levels and (2) reducing the fouling of boiler heat-transfer surfaces.

Both proprietary and pure compounds were found to be equally effective. Thus, if additives are used, cost savings can be maximized by using pure compounds which are less expensive.

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SECTION 1

INTRODUCTION

For over 125 years, manufacturers of additives have claimed that improved performance of combustion equipment can be achieved by adding various proprietary materials to the fuel or the flame. The aim of additive utilization has varied through these years depending largely on the problem area of interest at that time. Earlier interest was focused on additives to minimize corrosion and deposits on heat transfer surfaces. The current concern in limiting air pollution has stimulated an interest in additives as a low-cost technique for reducing emissions. Now, with possible fuel shortages and increasing fuel costs, additives are being considered as a means to improve boiler efficiency.

While qualitative observations and commercial claims for the effectiveness of fuel additives in reducing emissions and increasing boiler efficiency are numerous, the effectiveness of some of these additives has been questioned because of the lack of consistent results in actual commercial usage. This inconsistency, in part, could be attributed to the methods utilized in field evaluation and, perhaps, to differences in combustion equipment, operation, and maintenance. Also, relatively few quantitative data are available from experimental investigations in which conditions are well defined and in which pertinent measurements have been made.

In an effort to establish the effectiveness of additives, the U.S. Environmental Protection Agency (EPA) conducted an in-house research program to evaluate about 300 fuel additives as to their potential for reducing various emissions from distillate-fuel fired residential furnaces (1). The results were variable, but a number of additives were found to reduce particulate emissions and smoke. A second EPA program examined the effectiveness of several fuel additives in reducing SO_2 when firing residual oil, but none were found to be effective for SO_2 control (2).

This investigation extends those programs to larger combustion systems, with emphasis on the evaluation of combustion additives used for residual fuel oil. Of particular interest was the determination of additive effectiveness in reducing smoke and particulate emissions, including polycyclic organic matter (POM). The Federal Energy Administration, by funding through this EPA contract, has extended the study to include evaluation of additives as a means of increasing overall boiler efficiency, and, thus, conserving fuel.

Other aspects of this program, reported elsewhere, include:

- State-of-the-art review of combustion additives for pollution control (3). Appendix A contains the summary and conclusions from this report.
- Experimental studies to investigate NO_x formation in CO flames (4).

This report combines both the EPA and FEA aspects of the study and includes pertinent information from the reports mentioned above.

SECTION 2

OBJECTIVE AND SCOPE

The objective of this experimental research program was to provide a controlled and documented evaluation of the effectiveness of proprietary combustion-type fuel-oil additives and pure compounds for reducing air pollutant emissions and for increasing boiler efficiency. This research investigation focused on those combustion additives intended to improve combustion and reduce smoke and particulate emissions by their action in the combustion or flame zone. Although it is recognized that fuel-handling additives (intended to improve the handling or storage characteristics of the fuel) and post-flame treatment additives (intended to control corrosion and deposits on boiler surfaces) can be effective in maintaining burner performance and boiler efficiency, these types of additives were not systematically studied in this program. An exception to the above statement are the organo-metallic compounds which are used as both combustion-improver and post-flame-treatment additives.

The experimental program was conducted in a commercial fire-tube packaged-boiler of 50 boiler horsepower capacity (500 kW) firing both distillate and residual oils. The boiler was tuned to operate at a baseline condition, such that smoke emission levels were representative of similar boilers observed during a field investigation of boiler emissions (5). At the baseline condition, the boiler was probably tuned to a better condition than most operating units in which combustion additives are tried (typically additives are not used unless the boiler operator is grasping for some means to meet emission or other criteria).

A total of 24 fuel additives of representative fuels were evaluated when firing residual oils at a continuous rate (thus producing constant-load operation). Eleven of the additive types were also evaluated when firing distillate oil. In addition, some additives were evaluated under cyclic operation, variable load, and with a detuned burner so that the effectiveness of additives could be assessed as a function of these operating parameters. The majority of the evaluation runs were "short-term" in that emission data were obtained over a 2-hour period. Also, several "long-term" runs were conducted in that data were obtained over a 60 to 80 hour period to assess possible improvements in boiler efficiency.

Gaseous and particulate emissions were measured for baseline and additive runs. For many runs, sampling and analysis for POM emissions were conducted, and for a few runs, the particle size of particulate emissions was determined.

SECTION 3

SUMMARY OF RESULTS

The principal results of this experimental research investigation can be summarized as follows:

- Alkaline-earth and transition metal additives used in concentrations of 20 ppm to 50 ppm of metal in residual oil were effective in reducing carbon particulate emissions by as much as 100 percent. However, data suggest that, for burners having higher emissions in the baseline condition, higher additive concentration would be required to achieve the same level of effectiveness.
- Additives, both proprietary and pure compounds, containing certain alkaline-earth and transition metals were effective in increasing the efficiency of a boiler fired with residual oil (without increasing emissions) by reducing stack loss through (1) permitting boiler operation at lower burner excess-air levels and (2) reducing the fouling of boiler heat-transfer surfaces. For the 50-bhp (500 kW) boiler during 80-hour runs, a gain in efficiency of 2 percent was achieved, approximately half from reduction in excess air levels and half from reduction of fouling. This does not imply that such an increase could be

realized under all field conditions and definitely would not be achieved without appropriate boiler adjustment.

- Optimum savings in fuel costs could be realized by utilizing pure compound combustion additives in this boiler. Proprietary additives, used at effective concentrations, cost at least twice that of the most effective pure compound additives and, thus, tend to reduce the savings realized from burning less fuel. With a typical current market price of oil ($.30/gal), utilization of pure compounds would be cost effective when an incremental gain in boiler efficiency of at least 0.6 percent is realized. For the least expensive proprietary additive, an incremental gain in boiler efficiency of at least 1.5 to 2 percent would have to be realized before they could economically be justified.
- The alkaline-earth and transition metal additives were also observed to be effective in reducing emissions of smoke and polycyclic organic matter.
- These additives appeared to be equally effective in reducing particulate emission levels from a tuned and detuned burner. However, they appeared to be less effective for reducing smoke from detuned burners.
- In cyclic operation where particulate and POM emissions were higher than steady-state operation, additives were more effective in reducing POM than particulates.
- The use of metal-containing additives in combustion systems that generate little or no carbon particulate, such as well-designed and maintained boilers firing distillate oil, could result in higher particulate emissions due to the added metallic components.
- Additives effective in reducing carbon particulate emissions were observed to reduce the equivalent aerodynamic mass mean diameter of particles. Overall, the mass of particulate emission in the respirable range was reduced by these additives.
- No additive was found to be effective in reducing either nitrogen oxides or sulfur oxides emissions.
- CO emission levels (<15 ppm) and gaseous hydrocarbon emission levels (<10 ppm) for the baseline

condition were almost negligible so that there
was no potential for additives to be effective
in reducing these emissions.

Although additives were effective in reducing particulate emissions, alternate means for control of particulate emissions and boiler efficiency must be recognized. Utilizing existing burner technology to achieve improved air-fuel mixing and careful attention to boiler maintenance may be more cost effective than the use of fuel additives.

SECTION 4

SIGNIFICANCE AND LIMITATIONS OF THE RESULTS

The results of this study indicate that additives can be effective in promoting carbon burnout, providing the combustion conditions are not otherwise conducive to complete carbon burnout. The extent of carbon particulate reduction for any specific boiler would be dependent upon the interrelation among the specific boiler and burner design features, fuel, and the additive type and additive dosage.

Although criteria identifying the specific additive and concentration for all types of oil-fired boilers were not developed, it is reasonable to assume that the results of this study can be applied to most systems, as the mechanistic effects of additives are not restricted to a specific type of combustion system. However, for additives to be effective in increasing efficiency, the potential must exist to decrease stack loss by a reduction in excess air level and/or a reduction in the fouling of heat transfer surfaces.

With technological advances and modern equipment designs, it is possible to achieve relatively low carbon particulate emissions and boiler efficiencies near 85 percent without the use of additives. This performance is realized by the use of: state-of-the-art burners, most of which are capable of satisfactorily operating at excess air levels less than 15 percent [and some utility boilers even as low as 1 percent (6)], while generating little or no smoke or carbon particulate; economizers and air preheaters that lower stack gas exit temperatures below 350 F (177 C); and soot blowers to remove deposits from heat transfer surfaces. It is unlikely that additives would be effective in improving efficiency or reducing emissions from such systems. However, in terms of the overall economics, these optimum efficiency designs cannot be justified for every boiler installation. In addition, there are many existing boilers that were marginally designed or are poorly maintained and, thus, generate relatively high levels of particulate and which operate at relatively low efficiencies. It is in these systems that the results of this study indicate that consideration could be given to the use of additives. However, before additives are used, it is recommended that the burners be tuned to achieve optimum performance which may alleviate any need for an additive.

The results of these studies indicate that additives can be effective in promoting carbon burnout and, thus, permit operation at increased efficiency. The exact incremental gains in efficiency for any specific boiler would be dependent upon the interrelation among such factors as the specific boiler design, fuel used, and the additive type and additive dosage. For the boiler system, the controlling factor for additive effectiveness is not the type of boiler system itself (whether it is fire-tube or water tube). Rather the important factors are the conditions in the preflame, flame, and immediate postflame regimes as governed by the design and operation of the burner. The physical and chemical properties of the oil have an effect on the character of the particulate. Also, certain impurities and trace elements in the oil may affect the mechanistic action of the additive. Thus, if additives are to be used, the type and concentration will be dependent upon the design and operation of the burner and by the fuel used.

SECTION 5

BACKGROUND

ADDITIVE TYPES

In the course of the development of oil-firing technology, additives have been developed for a variety of purposes. As shown in Table 1, these additives can be divided into three general classes, according to their function:

Class I. Fuel-handling additives
Class II. Combustion additives
Class III. Postflame treatment additives.

TABLE 1. CLASSES OF ADDITIVES BY FUNCTION IN OIL AND COAL COMBUSTION SYSTEMS

CLASS I. FUEL-HANDLING ADDITIVES	CLASS II. COMBUSTION ADDITIVES	CLASS III. POST-FLAME TREATMENT ADDITIVES
For Improved Storage and Handling	For Improved Combustion and Pollutant Reduction	For Post-Flame Treatment
Fuel stability additives - Sludge and gum inhibitors - Detergents - Metal deactivators - Color stabilizers Flow improvers - Pour-point depressants Demulsifying agents Anti-static additives Anti-icing compounds Corrosion inhibitors (for tank protection)	Combustion improvers - To reduce smoke or particulates - To reduce CO, hydrocarbons, or polycyclic organic matter Additives to alter particulate size or character Additives to reduce formation of pollutant gases - Nitrogen oxides, NO_x - Sulfur trioxide, SO_3	Soot removers (from heat-transfer surfaces) Additives to control fireside corrosion or slag deposits Additives to enhance particulate collection in electrostatic precipitators SO_x scavengers

Class I Additives--

The fuel-handling additives may be considered those whose purpose is to insure the quality of the oil in storage and handling -- up to the time it is delivered to the burner. Consequently, this class of additives includes: (1) antioxidants, which prevent deterioration of the oil by reaction with oxygen during storage, (2) pour-point depressants, which reduce oil viscosity for ease of handling, (3) corrosion inhibitors, which prevent contamination of the oil by rust from the storage tanks, (4) metal deactivators, which tie up trace metals that catalyze oil deterioration, and (5) miscellaneous additives for such functions as sludge dispersant or water emulsification. These additives are usually mixtures of complex organic compounds in a suitable solvent for introduction into the oil. A review of these additives is contained in Appendix B.

Class II Additives--

Combustion additives are intended to reduce the amounts of pollutants formed during combustion, or to convert the pollutants into easily removable solids. A variety of organic, organometallic, and inorganic compounds have been tried for this purpose and it has been found that the organometallics are most effective, particularly in view of the relative ease of introduction into the fuel. These compounds introduce a metal which either acts as a catalyst for the combustion reaction, or promotes free radical formation that inhibits pollutant-developing reactions. The organic portion of the additive molecule provides the needed solubility in the oil and also influences the stability and volatility of the additive. Such additives are effective in reducing the unburned carbon in the particulate emissions. Since they affect the carbon combustion, they may also be capable of reducing the amount of polycyclic organic matter formed during combustion.

Little effect of combustion additives has been found on gaseous pollutants such as nitrogen oxides or sulfur oxides. A summary of technical literature relating to Class II additives is contained in a separate report -- "Combustion Additives for Pollution Control - A State of the Art Review" (3).

Class III Additives--

Post-flame treatment additives include various scavenging agents, pollutant property modifiers, and agents that modify the catalytic properties of exposed heat exchanger and breeching surfaces. However, the development of additives to reduce corrosion has received the most attention. These corrosion additives are aimed at reducing the corrosive attack of combustion gases and fly ash on the heat transfer surfaces of the boiler. [A summary of corrosion additives intended for fireside corrosion control is contained in Reid's Monograph on external corrosion and deposits (7).]

Class III additives are primarily alkaline materials either formed by oxidation of a metal in the flame or added at some point after the combustion zone. Their action is to neutralize the sulfur oxides in the flue gases and any sulfuric acid which might be condensed from the gas stream in regions of the boiler where the temperature falls below the acid dewpoint. Compounds of magnesium, calcium, and zinc have proven most useful for this purpose. In the case of magnesium, it also serves to reduce corrosion from vanadium by forming vanadates with high melting points. As in the case of the combustion additives, the most effective corrosion additives are the organometallic compounds which can be readily dissolved in the fuel. (Additionally, certain of these organometallic compounds can be considered as both Class II and Class III type additives.)

REVIEW OF LITERATURE REGARDING EXPERIMENTAL ADDITIVE INVESTIGATIONS

To guide the selection of additives for this program, the literature pertaining to experimental studies of combustion additives was reviewed (3). Previous investigators have used a wide variety of organic, organometallic, and inorganic compounds in efforts to reduce the amounts of pollutants formed during combustion, or to convert the pollutants into easily removable solids.

The greatest amount of effort in additive development has been devoted to particulate emissions. This emphasis has been the result of the almost universal recognition of smoke as an undesirable emission over a period of many years. For obtaining reduction in particulate formation in fuel-oil combustion processes, experimental evidence indicated that compounds of the transition metals, manganese, iron, nickel, and cobalt, could be effective (8). The alkaline earth metals, barium and calcium, also gave evidence of useful activity (9,10). The best results were obtained with organometallic derivatives of these metals. The organic portion of the molecule provides the needed solubility in oil and also influenced the stability and volatility of the additive molecule.

Only a few investigations have examined the effect of additives on potential carcinogenic materials in the particulate emissions, but this aspect is presently receiving a significant amount of attention. Such potential carcinogenic agents are found, primarily, in the POM that forms during the combustion of the fuel (11,12). Most of the early research was done with gas flames or light fuel such as distillate oil. The additives which were reported as effective in reducing the POM emissions included organic compounds such as nitroparaffins and peroxides (13), as well as organometallic compounds of manganese and iron (14). Although the physical state of POM and the carbonaceous portion of the particulate is different, their probable common origin and chemical reactivity suggest that an additive effective for one would have some effect on the other. This result was generally observed in earlier diesel engine studies, and where both types of emissions were measured, the POM usually was reduced to a greater extent than was the particulate (13). [It should be noted that the techniques used in the collection and analysis of POM compounds have undergone extensive development since these early studies. These early POM determinations usually were reported as only one or two species, such as benz(a) pyrene, while current techniques scan for approximately 18 species during analysis. In addition, some of the POM emissions that have been reported in the literature use the BaP emission as the key to which a constant factor is applied to predict total POM levels. The data contained in this report and another EPA program (EPA Contract No. 68-02-1848) indicate this method of predicting total POM is somewhat questionable, as the ratio of the BaP emission to the total POM emissions varies considerably.]

A previous EPA program involved tests of numerous commercial additives used with distillate heating oil in a residential oil burner (1). In general, the additives were found to have a minor effect compared to the opportunity for emission control by proper adjustment and operation of the burner. However, the additives containing manganese, iron, or cobalt did reduce the particulate emissions. A few organic formulations containing no metals gave moderate reductions in particulates, but the concentrations of the additives required were too high to be practical. No changes were observed in the amounts of nitrogen oxides or sulfur oxide emissions with any of the additives.

Another EPA program was an investigation of the effectiveness of several proprietary fuel-oil additives in reducing sulfur oxide emissions when firing residual oil in a commercial boiler (2). No effects of the additives were found for sulfur oxide emissions or for nitrogen oxides.

The experience of the EPA investigators with the inefficacy of additives for reducing the nitrogen oxides or sulfur dioxide in the emissions, verified the generally negative results reported in earlier literature (3). Only in the case of sulfur trioxide, which is present to the extent of 25 to 30 ppm in the flue gases, has an additive effectiveness been demonstrated at reasonable additive concentrations. Chemicals which form basic oxides such as magnesium, calcium, and zinc have reduced sulfur trioxide levels substantially (15). One area of particular concern was whether the various additives which did result in reduced SO_3 did so by oxidizing the pollutant into metallic sulfate.

BASIS FOR EFFICIENCY GAIN BY ADDITIVE UTILIZATION

The efficiency of a boiler can be expressed as:

Boiler Efficiency = 1 - (Combustion Loss) - (Miscellaneous Loss) - (Stack Loss).

Oil-fired boilers operating at any acceptable condition have low concentrations of CO, unburned carbon, and unburned hydrocarbons in their stack gases and consequently have negligible combustion losses. The miscellaneous loss, insofar as it is real rather than the accumulation of errors in the boiler heat balance, represents the heat loss from the external boiler surface or jacket. Typically, miscellaneous losses are a few percent. Clearly, additives have no effect on combustion losses or miscellaneous losses.

The stack loss represents the heat carried away in the stack gases, the largest loss in heat (and thus efficiency) for the boiler. Stack losses are typically between 15 and 30 percent of the heating value of the fuel. Stack loss is numerically equal to

> (mass of stack gas) x (specific heat of stack gas) x (stack temperature - ambient temperature) + (latent heat of the moisture formed from the hydrogen in the fuel).

The mass of stack gas is equal to the mass of the products of stoichiometric combustion plus the mass of excess air. The stack temperature is determined by the amount of heat transfer surface in the boiler and the effectiveness of this surface, the effectiveness being decreased by fouling with soot and particulates, and reduced residence time accompanying higher excess air levels.

Combustion additives that effectively control smoke and particulate can influence the stack loss both directly and indirectly. The direct effect results from the reduced fouling of heat exchanger surfaces consequent to the reduced smoke and particulate levels, and possibly through some change in the characteristics of the particles which reduces their fouling tendency. The indirect effect is a result of the fact that the minimum acceptable excess air level, at least in commercial and small industrial oil-fired boilers, is controlled by the maximum acceptable smoke density, typically a Bacharach Smoke Number of 4 (16). Thus, a combustion additive that reduces the smoke density will permit operation at lower excess air levels without exceeding the maximum acceptable smoke density.

The efficiency gain that can be obtained through these mechanisms cannot exceed the stack loss (about 20 percent in typical operation) and, in fact, is limited to a fraction of this loss. Thus, a well designed and

and maintained commercial boiler firing residual oil may operate at an excess air level of 20 percent. If such a boiler could be fired at the stoichiometric fuel-air ratio, the incremental gain in efficiency (reduction in stack loss) could be due to the reduced mass of stack gas would be about 2 percent. (Obviously the gain would be higher for a poorly maintained unit operating at a high excess air level.) The accompanying reduction in stack loss due to the reduced gas velocity and increased residence time in the boiler cannot be conveniently calculated but is relatively smaller. The gain in boiler efficiency that can be achieved by reduced fouling of the heat transfer surfaces is dependent on the boiler maintenance (frequency of cleaning) but may represent about 1 percent under reasonably typical conditions.

The results of the study conducted for FEA show that combustion additives that reduce stack-gas particulate loadings are generally effective in reducing the smoke density and visa versa. Thus, those combustion additives found effective as pollution controls may also be expected to be effective in promoting the achievement of higher boiler efficiency.

FACTORS AFFECTING BOILER EFFICIENCY

For a given boiler, additional heat transfer surface (such as economizers and air heaters) can be added to increase efficiency. However, the only operating variables that can be controlled by the boiler operator or serviceman are mass of excess air and heat exchanger cleanliness.

Excess Air

Figure 1 indicates an approximate relation between stack gas loss (or incremental gain in boiler efficiency) and stack gas temperature for several excess air levels. Excess air levels of less than 15 percent can be achieved with modern burner design (17), although there are a significant number of boilers operating at substantially higher excess air levels. Typical excess air levels vary with the size of the unit, with the smaller units having less sophisticated controls or operator attention and, thus, operating at higher excess air levels than the larger units. It is

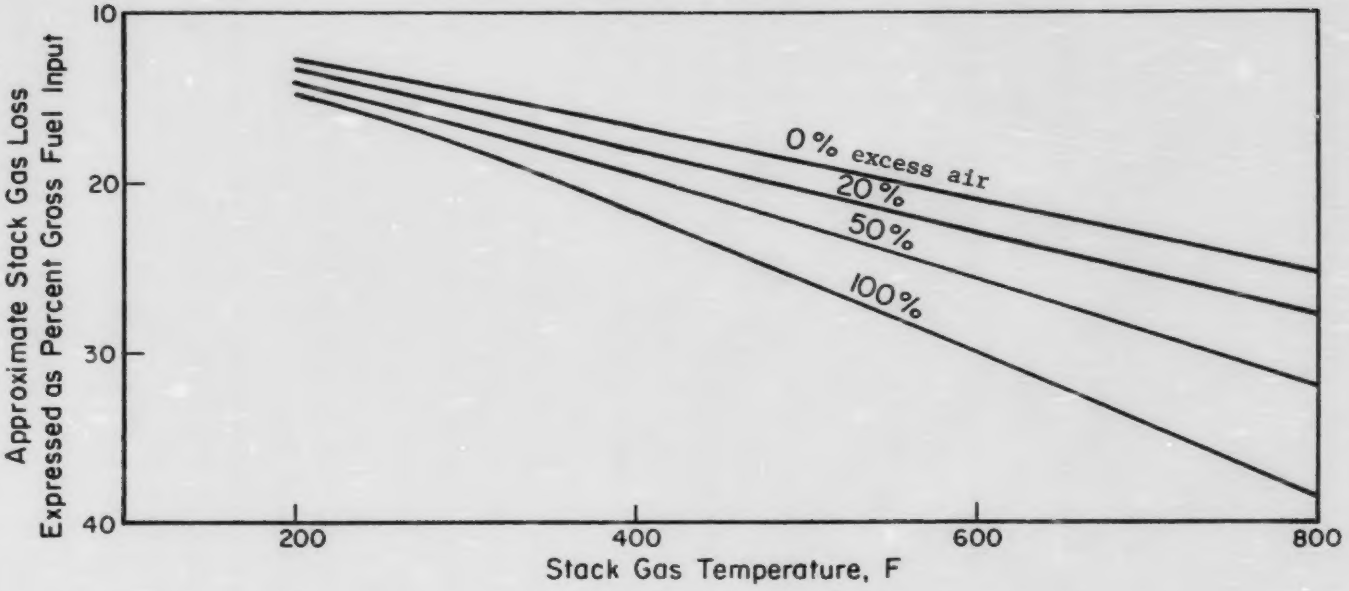

FIGURE 1. APPROXIMATE STACK GAS LOSS AS A FUNCTION OF STACK GAS TEMPERATURE

estimated that typical excess air levels in the field run approximately as follows (18).

Capacity	Percent Excess Air
Less than 100 bhp (1 MW)*	50
100 bhp (1 MW) to 60,000 pph** (17 MW)	35
Greater than 60,000 pph	15

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* pph = pounds per hour of steam generated.
** MW refers to thermal rather than electrical.

Accordingly, the greatest potential for increasing boiler efficiency by reducing excess air would be for those boilers having capacity of less than 60,000 pph. Many of these boilers could be "tuned" to operate at lower excess air levels, but the actual level would be dependent on the specific boiler installation and its operational and maintenance procedures.

Heat Transfer Surface

From Figure 1 (at 20 percent excess air), the incremental gain in boiler efficiency is about 2-1/2 percent for each 100 F reduction in stack gas temperature. The temperature of the stack gas leaving the boiler (not including heat recovery equipment such as economizers and air preheatrrs) is partially determined by the saturated water temperature corresponding to the boiler operating pressure. Typically, for low-pressure boilers, the stack gas temperature is about 500 F (260 C) and would be proportionally higher as the boiler operating pressure increases. The removal of heat from products of combustion becomes expensive after the stack gas temperature drops below 500 F (260 C)(19).

The use of additional boiler convection surface to recover (19) heat from flue gases at temperatures below 500 F (260 C) is usually impractical. However, economizers and air heaters can be included in designs or added on to systems that can economically justify heat recovery. The use of this equipment can lower stack gas temperatures below 250 F (177 C), and thus, achieve gains in efficiency of at least 3 to 5 percent for low-pressure boilers and 6 to 10 percent for high-pressure boilers (17). Historically, these types of heat recovery devices have been applied only to units with high load factors with capacities over 100,000 pph steam. However, the economizer has been found economically feasible in certain (high load factor) units with capacity as low as 30,000 pph (17), while the air heater becomes economical for some boilers with capacities as low as 50,000 pph (19).

EFFECT OF ADDITIVES: INCREASED EFFICIENCY VERSUS REDUCED EMISSIONS

The improved combustion achieved by using additives can be translated into the following results:

(1) Reduced emissions of smoke and particulate and reduced fouling of heat transfer surfaces resulting in increased boiler efficiency

(2) Increased boiler efficiency by operation at lower excess air.

The benefits are somewhat competing and maximizing one reduces the other.

Figure 2 illustrates the effectiveness of additives on emissions and excess air. Assume Curve A is the smoke versus excess air curve of the boiler firing without additives and that Point X is the condition at which the boiler is operating. Also, assume that the use of an effective additive alters the smoke versus excess air relationship to that of Curve B. Now the boiler can be operated at Point Y with the same excess air as Point X, but with a reduction in smoke emissions and some small incremental gain in boiler efficiency because of reduced fouling. Also, the boiler can be operated at Point Z with the same smoke emission as Point X, but with a reduction in excess air and some reduction in fouling so that the incremental gain in boiler efficiency is greater than that achieved at Point Y. The boiler can be operated at some point between Point Y and Point Z, with some reduction in both smoke and excess air. However, the maximum reduction in emissions and the maximum reduction in excess air cannot be realized simultaneously.

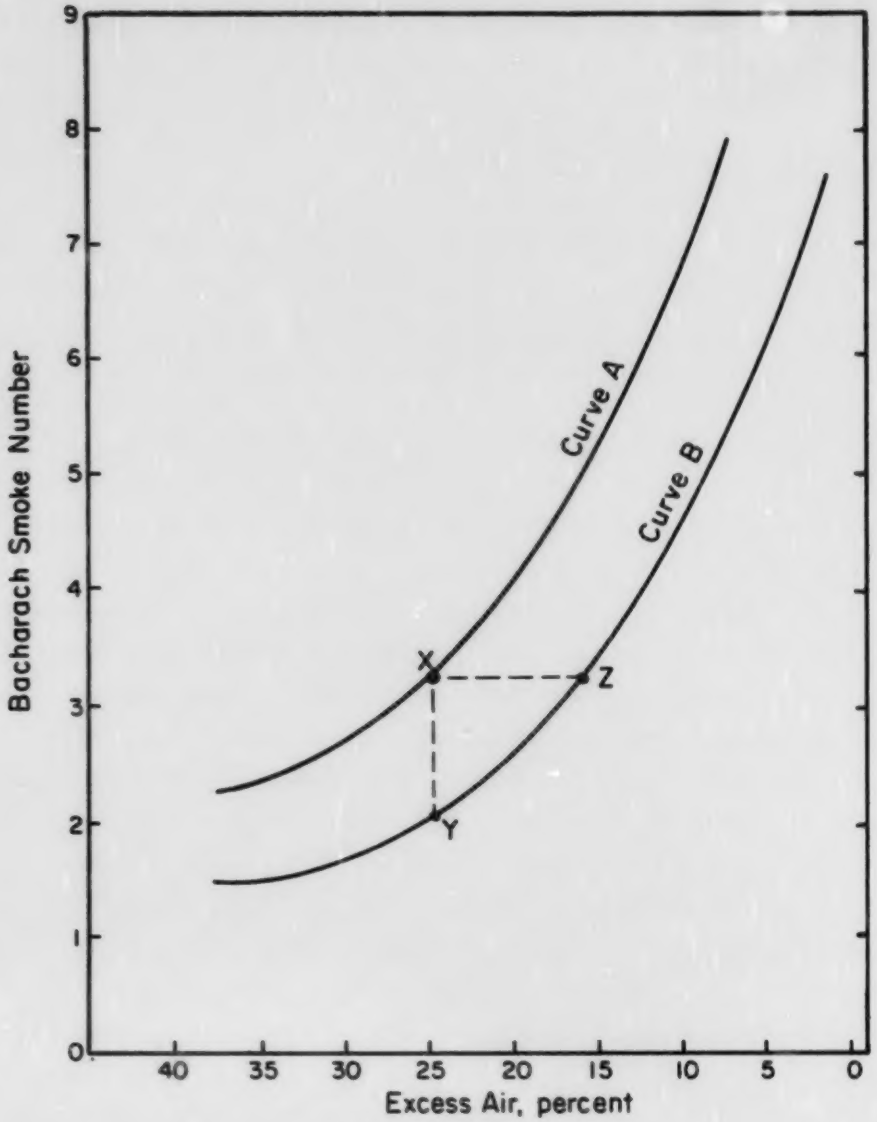

FIGURE 2. BACHARACH SMOKE VERSUS EXCESS AIR LEVEL INDICATING BOILER-OPERATING POINTS OF MAXIMUM SMOKE REDUCTION OR MAXIMUM INCREMENTAL GAIN IN EFFICIENCY

SECTION 6

PLAN OF EXPERIMENTAL INVESTIGATION

Proprietary and pure compound additives were evaluated in a modified commercial packaged boiler with both distillate and residual oil.

EXPERIMENTAL FACILITY

Figures 3 and 4 show the overall experimental facility. The basic element of this facility is a 50-bhp (500 kW) commercial fire-tube boiler capable of firing natural gas, distillate oil, and residual oil at rates up to 2 million Btu/hr (0.59 MW) and generating up to 1500 lb/hr (680 kg/hr) of steam at 15 psig (103 kN/m^2). A special sampling platform was erected over the boiler to permit sampling in a straight section of stack and facilitate overall sampling procedures.

Fire-Tube Packaged Boiler

Although fire-tube packaged boilers of the type used in this program are fully automated, some modifications in the 50-bhp (500 kW) boiler were made to provide greater flexibility and more accurate control in the operation of the boiler. The air and oil control linkages of the burner were disconnected so that combustion air-flow rates and fuel-flow rates could be controlled independently. Combustion air was metered through a thin-plate orifice and distillate oil flow rate with a rotameter. When firing residual oil, oil firing rate was determined from beam-scale readings.

Because a continuous fuel flow rate could not be maintained within a 2 percent range with the oil pump and preheater system supplied with the boiler, this assembly was replaced by a variable speed, positive-displacement gear pump and temperature controllers that could provide a constant fuel

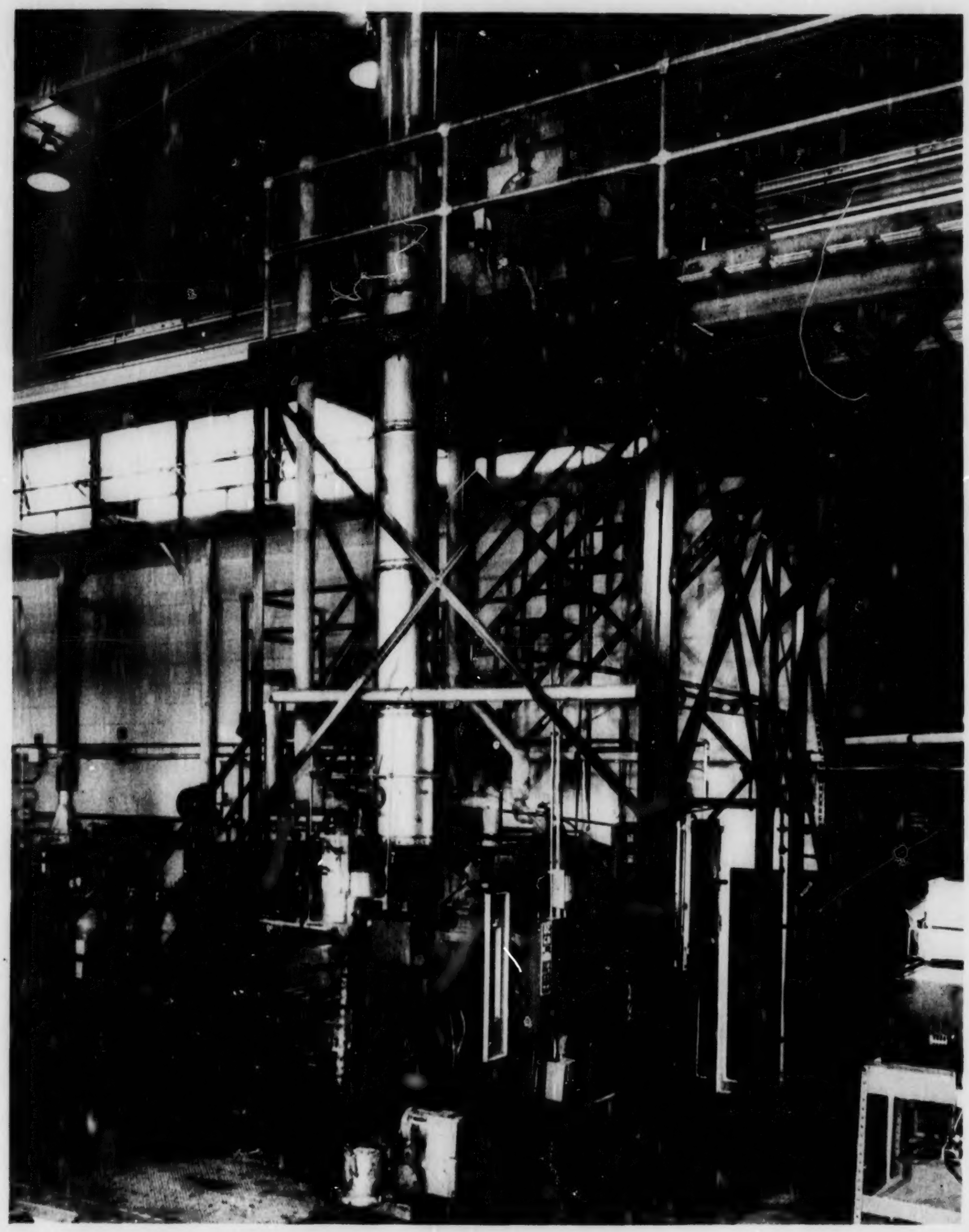

FIGURE 3. EXPERIMENTAL 50-BHP RESEARCH BOILER FACILITY

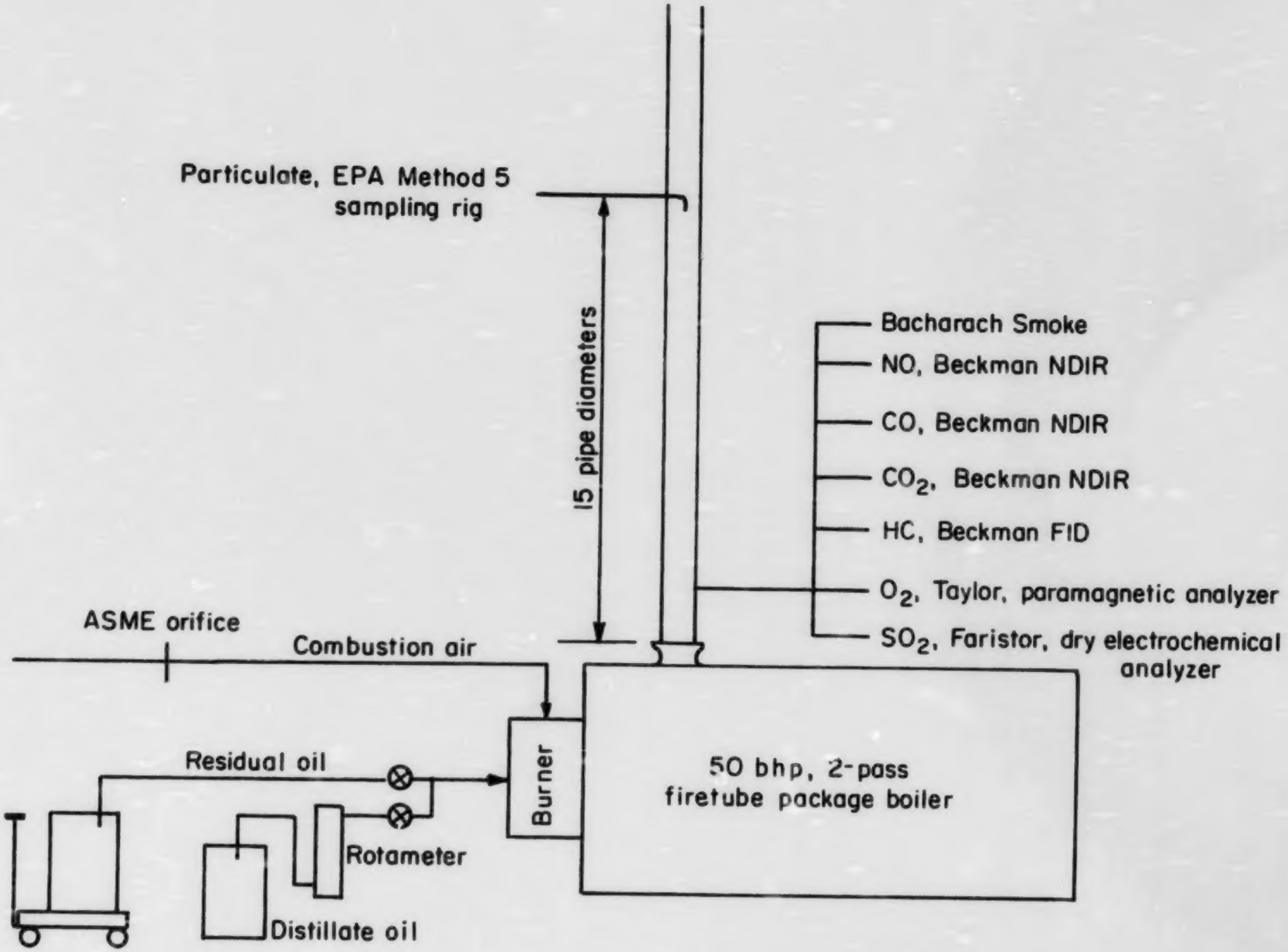
Particulate, EPA Method 5
sampling rig
15 pipe diameters
Bacharach Smoke
NO, Beckman NDIR
CO, Beckman NDIR
CO_2, Beckman NDIR
HC, Beckman FID
O_2, Taylor, paramagnetic analyzer
SO_2, Faristor, dry electrochemical analyzer
ASME orifice
Combustion air
Burner
50 bhp, 2-pass
firetube package boiler
Residual oil
Rotameter
Distillate oil

FIGURE 4. SCHEMATIC OF EXPERIMENTAL FACILITY

temperature and delivery rate to the burner nozzle. With this system, air/fuel ratios and firing rates remained constant within 2 percent throughout the duration of an experimental run.

Sampling Platform

A sampling platform was erected above the boiler outlet to permit sampling in a straight section of the 12-inch (0.30 m) diameter insulated stack, 15 pipe diameters downstream of the boiler outlet. At this location, velocity and temperature profiles (measured with a hot-wire anemometer and thermocouple) were flat so that traversing was not necessary during particulate sampling.

SELECTION OF ADDITIVES

This investigation, as indicated previously, was confined to fuel additives that were intended to improve combustion. Pure compounds as well as proprietary additives were considered so that a broad range of materials could be evaluated. However, the selection of additives was restricted to materials that when burned would not generate new toxic pollutants or increase the levels of those already present. Accordingly, compounds containing nitrogen, sulfur, or metals known to be toxic were not considered. Likewise, compounds required to be used at impractical concentrations (over 1 percent by weight) were rejected.

Additive Types

Combustion additives can be categorized as

- Organometallic
- Organic
- Inorganic.

Table 2 categorizes the additives used in this study according to defined types and subtypes. Inorganic additives were not evaluated because of their insolubility in oil. The additives listed in Table 2 were selected on the basis of the results of an earlier EPA study (1) and a state-of-the-art review of additive technology that included theoretical considerations of the mechanism of pollutant formation and possible modes of additive action (3).

TABLE 2. COMBUSTION ADDITIVES SELECTED FOR EXPERIMENTAL STUDY

ORGANOMETALLIC	ORGANIC
Naphthenates	Hydrocarbon
Cobalt	LSD (C_7H_8, trace metals)
Iron	Improsoot (C_7H_8, trace metals)
Manganese	
Barium	Triple E
Iron + barium	
Zinc	Toluene (C_7H_8, pure hydrocarbon)
Calcium	Watcon 130 (trace metals)
Cyclopentadienes	Ether
Manganese - CI-2 (24 % Mn)	Diglyme
Iron - Pd 1654 (1% Fe)	
	Alcohol
Sulfonates	
	Ethyl
Barium	Hexyl
Ethyl Hexoate	Acid
Barium	Napthenic
	Ethyl hexoic
Carbonyls	
Iron	
Other	
MC-7 soluble (3.6% Mn, 3% Ba)	
Rolfite 404 (2% Mn)	

Additive Concentrations

Initially, additive concentrations were based on those reported in the literature (3); for proprietary additives, the concentrations were those recommended by the additive manufacturer. The results of the earlier additive evaluation runs then became the basis for selection of additive concentrations for later runs. For pure compounds, additive concentrations were based on introducing sufficient amounts of the additive to obtain 27 ppm of metal in the oil (0.1 g metal/gal of fuel oil). For a limited number of these compounds, concentrations were varied from 5 ppm of metal up to 100 ppm metal in the oil to determine the relation between concentration and the effectiveness of an additive. In addition to the manufacturer's recommendation several proprietary additives were evaluated at concentrations corresponding to about 20 to 50 ppm of metal in the oil.

FUELS

Additives were evaluated with both distillate and residual fuel oils. The major effort of research, however, was conducted with residual oils and included both a 1 percent sulfur and a 2 percent sulfur oil. To provide a relatively consistent fuel oil supply, each of these oils was procured in 5000 (18.9 m^3) to 6000 gallon (22.7 m^3) lots and stored in 55 gallon (0.21 m^3) drums. A second shipment of the 2 percent sulfur oil was required to complete the long term evaluation runs. Table 3 lists some of the properties of these fuels.

TABLE 3. C-H-N-S AND ASH CONTENT IN WEIGHT PERCENT OF THE FUELS USED IN THIS PROGRAM

Fuel	API Gravity, °	Viscosity @ 122 F, ssf	Nominal Sulfur Content, %	C	H	N	S	Ash
Distillate oil	35.4	--	--	86.4	13.6	--	<0.1	<0.01
Residual oil	15.1	80	1	87.5	11.1	0.31	0.95	<0.04
Residual oil	13.2	100	2	88.4	10.4	0.5	1.75	0.020
Residual oil(a)	13.2	100	2	87.9	10.9	0.5	1.40	0.018

(a) Second load.

EXPERIMENTAL PROCEDURE

To provide a controlled and valid evaluation of each additive, specific experimental procedures were developed to minimize operational variations over the entire period of experimentation.

Basis for the Selection of Baseline Condition

To provide a realistic condition to evaluate additives, the boiler was tuned to produce a characteristic smoke curve representative of those generated from other commercial boilers (5). The tuning consisted of altering the mixing pattern of the burner by removing one of the diffuser rings.

Figure 5 shows the characteristic smoke curves of the 50-bhp test boiler and the average of several commercial boilers firing a residual oil. [This residual oil was not the same oil used in this program but was the reference fuel used in obtaining the boiler smoke data on EPA Contract No. 68-02-0251 (5)]. Figure 6 is a curve of particulate loading as a function of CO_2 (air/fuel ratio) for a constant firing rate. From earlier investigations (3), it was determined that additive action was only effective on carbon particulate only. Accordingly, additives were evaluated at a combustion condition that generated carbon particulate. The air/fuel ratio corresponding to 12.8 percent CO_2 was selected as one that generated a sufficient level of carbon particulate yet was insensitive enough so that small changes in air/fuel ratio did not produce a significant change in particulate emission level.

Particulate consists of two basic components: (1) an ash component originating with the fuel and (2) a carbon component resulting from incomplete combustion. When additives containing an ash (i.e., metal containing additives) are used, this ash becomes a third source of particulate in the stack gases. For combustion at a constant air/fuel ratio, the ash loading in the products of combustion (due to fuel ash) should be constant, assuming no accumulation on the boiler surfaces; the carbon loading could vary depending upon the completeness of combustion.

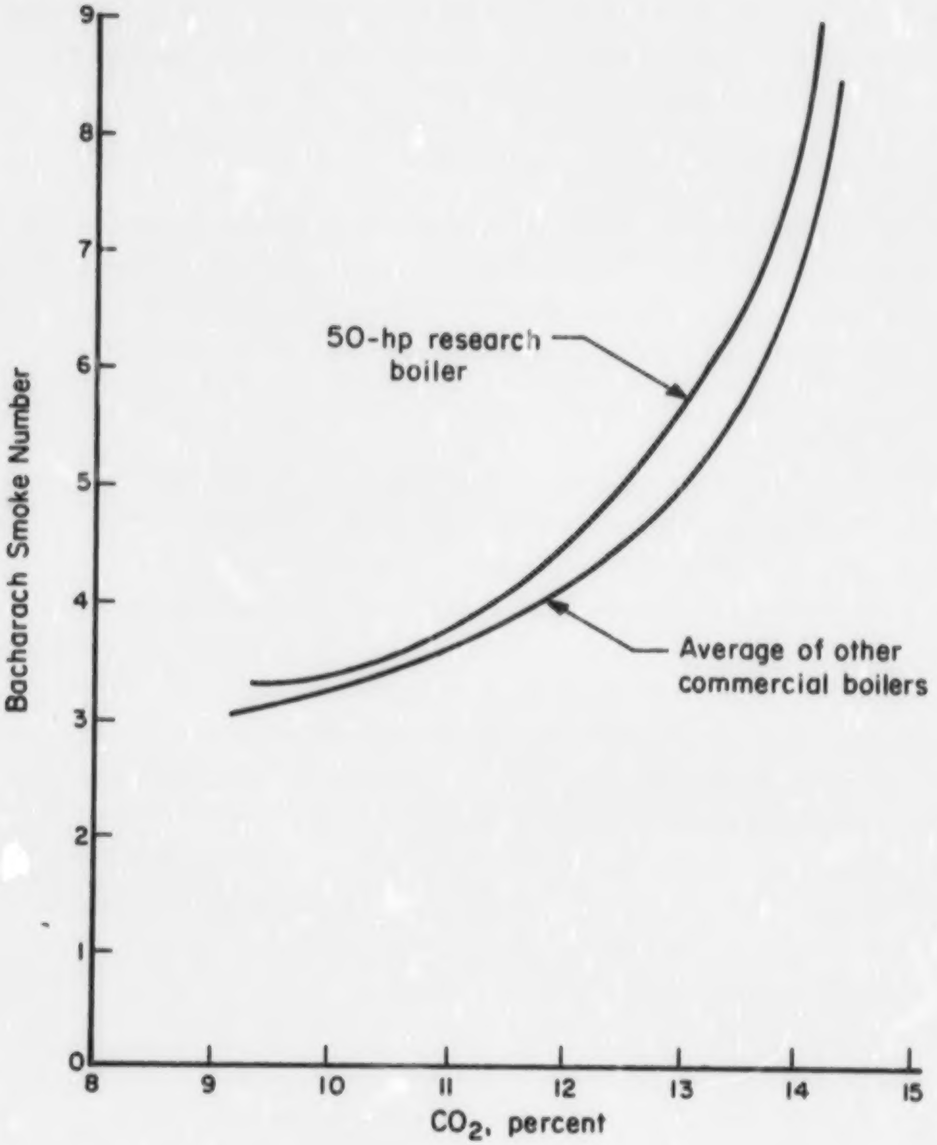

FIGURE 5. SMOKE EMISSION AS A FUNCTION OF CO_2 FOR 50-BHP RESEARCH BOILER AND THE AVERAGE OF SEVERAL COMMERCIAL BOILERS(5)

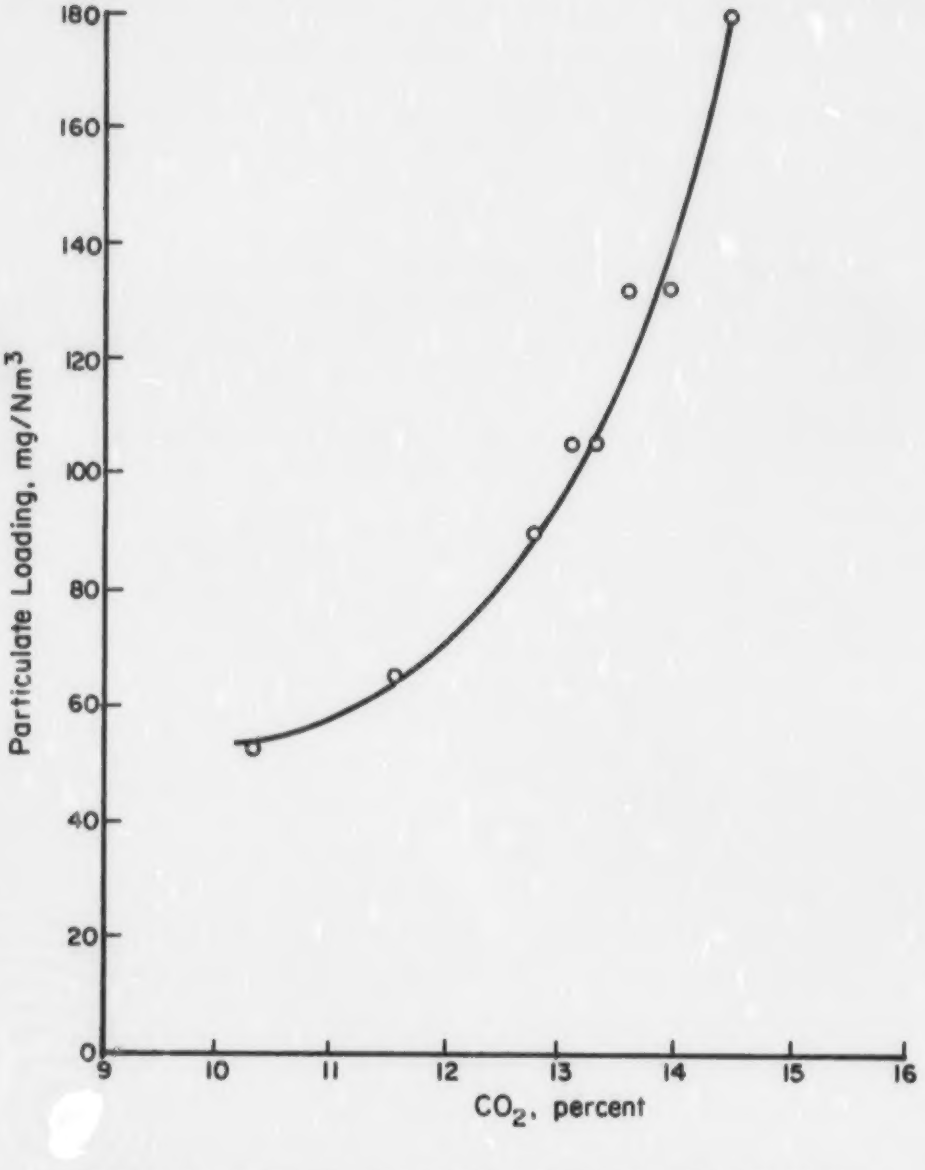

FIGURE 6. PARTICULATE LOADING VERSUS CO_2 FOR THE 50-BHP BOILER FIRED WITH RESIDUAL OIL

To minimize the variation in ash loading, all particulate measurements were made at the same air/fuel ratio corresponding to 12.8 percent CO_2 (about 20 percent excess air). A baseline firing rate of 80 lb/hr (36 kg/hr) was selected to correspond to a boiler load of 80 percent, identified by ABMA as being typical of field operation of commercial boilers (5).

Baseline and Additive Evaluation Runs

In general, each additive was evaluated from runs made on one day as follows:

(1) The reference fuel oil was fired at a constant rate in the boiler facility, and gaseous and smoke emission data were obtained over a range of air/fuel ratios.

(2) Filterable particulate emission (probe and filter catch only) was determined at one selected air/fuel ratio.

(3) The additive-containing fuel was then fired at the same firing rate over the same range of air/fuel ratios to generate a boiler performance curve with the additive corresponding to (1).

(4) A particulate sample was obtained with the additive-containing fuel ratio as for (2) above. Thus, the effectiveness of each additive could be determined by comparing the smoke and gaseous characteristic curves and the particulate loadings with and without additive for runs made on the same day. (Except as noted, all data reported in this report were obtained at steady state operation of the burner.)

The baseline run consisted of (1) and (2), and the evaluation run consisted of (3) and (4).

Burner Maintenance

At the completion of each day's experimentation, the entire fuel system was cleaned. The fuel nozzle was removed and cleaned in kerosine while the pump and fuel oil lines were purged with No. 2 oil. It was observed that if these maintenance procedures were not followed, over a period of several weeks the fuel nozzle would become fouled and burner performance would degenerate as indicated by the characteristic smoke curves of Figure 7. As a consequence, the baseline condition could have changed each day and all the additives could not have been evaluated under identical operating conditions. The gradual degeneration in boiler performance was attributed to plugging of the fuel lines by the residual

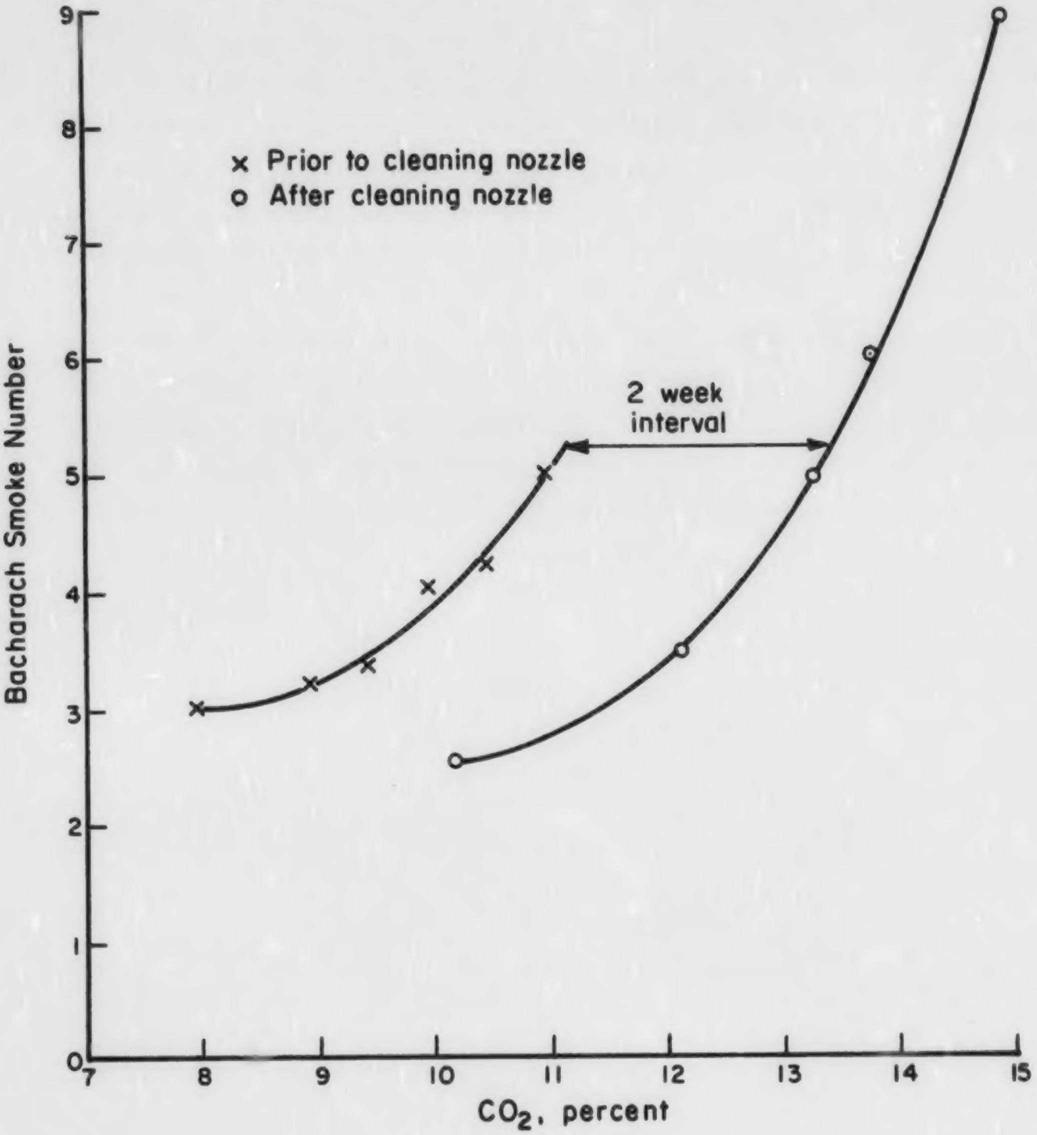

FIGURE 7. SMOKE EMISSIONS AS FUNCTION OF CO_2 FOR THE 50-BHP BOILER PRIOR TO AND AFTER CLEANING BURNER NOZZLE

oil remaining in the lines when the boiler was not to be used. No degeneration was observed during continuous operation of the boiler as the characteristic smoke curves were nearly identical at the beginning and the end of each baseline run including the long-term baseline run.

ANALYTICAL PROCEDURES

Particulate and POM samples were collected by a modified EPA Method 5 procedure with the probe wash and filter catch being used to determine the filterable particulate loadings and an adsorbent column being used to determine POM loadings (20). (The filter temperatures were 350 F rather than 250 F as in Method 5 to be compatible with POM sampling system.)

Flue gas constituents were determined by: paramagnetic analysis for oxygen; flame ionization detection for unburned hydrocarbons; nondispersive infrared for carbon monoxide, carbon dioxide, and nitric oxide; and a dry electrochemical analyzer for sulfur dioxide. Smoke emissions were determined with a Bacharach smoke tester according to the ASTM filter-paper method (D2156-65) for smoke measurements.

SECTION 7

EXPERIMENTAL RESULTS

The results of the additive evaluation runs in terms of the additive's ability to reduce particulate loadings and smoke levels in the stack are listed by fuel type in the following tables:

Table 4. Evaluation Runs With Distillate Oil

Table 5. Evaluation Runs With 1 Percent Sulfur Residual Oil

Table 6. Evaluation Runs With 2 Percent Sulfur Residual Oil.

Particulate emissions are listed in milligrams per cubic meter (mg/Nm^3) of flue gas at standard conditions. Smoke levels listed are for the additive evaluation run.

For the distillate oil runs, the boiler was fired continuously at approximately 80 lb/hr (36 kg/hr) at 14.0 percent CO_2. Likewise for most of the residual oil runs, the boiler was fired continuously at approximately 80 lb/hr (36 kg/hr) at 12.8 percent CO_2. However, as indicated in Tables 5 and 6 some runs were conducted at different conditions so the effects of additives at other modes of boiler operation could be examined.

The run numbers do not represent the chronological order in which the additives were run, but are presented in groupings of specific additive types or a specific set of boiler operating conditions. The additive concentrations or dosages are either designated as ppm metal in the fuel oil for the metal-containing additives, or by volume percent for the pure organic compounds. For organic compounds containing trace metals, both the weight percent of metal and volume percent of the additive are given.

TABLE 4. SUMMARY OF EVALUATION RUNS WITH DISTILLATE OIL

Run	Additive	Additive Dosage	Particulate Loading Additive mg/Nm^3	Particulate Loading baseline mg/Nm^3	Particulate Loading Ratio$^{(a)}$	Bacharach Smoke No. Additive$^{(b)}$
1	CI-2 (Ethyl Corporation)	27 ppm Mn, 0.0085% by vol.	14.4	13.6	1.0	2
2	MC-7 Soluble (Apollo Chemical)	27 ppm Mn, 20 ppm Ba, 0.079% by vol	16.9	12.9	1.2	1.5
3	Formula LSD (Commercial Chemical)	4 ppm Mn, 3 ppm Co., 0.079% by vol.	16.7	13.4	1.2	2
4	Rolfite 404 (Andrew Rolfe Co.)	4 ppm Mn, 0.022% by vol.	16.5	13.1	1.0	2
5	PD 1654 (Arapahoe Chemical)	5 ppm Fe, 0.047% by vol.	14.5	12.1	1.1	1.5
6	R-4000 (Triple E Products)	0.2% by vol. (no metal)	16.4	14.0	1.0	2
7	R-4000 (Triple E Products)	0.03% by vol. (no metal)	18.0	15.4	1.1	2
8	Watcon 130 (Industrial Chemical)	1.5 ppm Fe, 0.026% by vol.	16.2	16.6	1.2	1.5
9	Barium naphthenate	51 ppm Ba	22.0	16.6	1.6	0.5
10	Iron pentacarbonyl	27 ppm Fe	19.1	15.4	1.4	2.0
11	Cobalt naphthenate	27 ppm Co	16.0	11.8	1.2	2.0
12	Toluene	0.2% by vol.	17.8	14.7	1.3	2.0
		Arithmetic mean for baseline runs		14.1		

(a) The ratio of the particulate loading of the additive run and the arithmetic mean of the particulate loadings of the appropriate baseline runs.

(b) The Bacharach smoke number for the baseline run at 14 percent CO_2 was 2.

TABLE 5. SUMMARY OF EVALUATION RUNS WITH ONE PERCENT SULFUR RESIDUAL OIL

Run	Additive	Additive Dosage	Particulate Loading Additive mg/Nm^3	Particulate Loading Baseline mg/Nm^3	Particulate Loading Ratio$^{(a)}$	Bacharach Smoke No. Additive$^{(b)}$
	a. Evaluation Runs With Proprietary Additives					
13	MC-7 Soluble (Apollo Chemical)	27 ppm Mn, 20 ppm Ba, 0.08% by vol.	51.1	81.1	0.58	3
14	Formula LSD (Commercial Chemical)	4 ppm Mn, 3 ppm Co ,0.08% by vol.	77.0	79.5	0.87	3
15	Formula LSD (Commercial Chemical)	12 ppm Mn, 10 ppm Co, 0.2% by vol.	68.8	99.6	0.78	3
16	Improsoot (Commercial Chemical)	10 ppm Mn, 9 ppm Co, 2 ppm Ca	47.6	89.9	0.54	3
17	CI-2 (Ethyl Corp)	27 ppm Mn	100	86.3	1.13	3.5
18	CI-2 (Ethyl Corp)	27 ppm Mn	79.5	86.3	0.90	3.5
19	PD 1654 (Arapahoe)	5 ppm Fe	77.1	89.9	0.87	3
20	Watcon 130 (Industrial Chemical)	13 ppm Fe, 0.2% by vol.	66.1	87.2	0.75	3
21	Rolfite 404 (Andrew Rolfe Chem. Co)	4 ppm Mn, 0.02% by vol.	70.1	83.4	0.79	4
22	R-4000 (Triple E Products)	0.03% by vol. (no metal)	96.8	94.5	1.09	4.5
23	R-4000 (Triple E Products)	0.03% by vol. (no metal)	71.8	100.5	0.81	4
24	R-4000 (Triple E Products)	0.2% by vol. (no metal)	82.7	89.8	0.93	3.5
	b. Evaluation Runs With Pure Compound Organo-Metallic Additives					
25	Barium naphthenate	51 ppm Ba	50.5	91.8	0.57	2
26	Barium naphthenate	51 ppm Ba	48.6	116.6	0.55	2
27	Barium naphthenate	26 ppm Ba	61.4	83.3	0.69	2.5
28	Barium naphthenate	10 ppm Ba	72.7	85.0	0.82	3.5
29	Barium hexoate	40 ppm Ba	55.4	93.1	0.63	2
30	Cobalt naphthenate	20 ppm Co	50.5	91.8	0.57	3
31	Cobalt napthenate	27 ppm Co	60.5	89.1	0.68	3
32	Manganese naphthenate	27 ppm Mn	62.8	87.2	0.71	3
33	Iron naphthenate	27 ppm Fe	65.5	103.4	0.74	3
34	Iron pentacarbonyl	27 ppm Fe	63.5	84.3	0.72	3.5
35	Iron and barium naphthenate	27 ppm Fe, 51 ppm Ba	45.2	88.6	0.51	2
36	Iron naphthenate	11 ppm Fe	58.3	88.6	0.66	3
37	Zinc naphthenate	27 ppm Zn	86.9	94.5	0.98	4
38	Calcium naphthenate	27 ppm Ca	50.4	94.5	0.57	1.5

(continued)

TABLE 5 (continued)

Run	Additive	Additive Dosage	Particulate Loading		Particulate Loading Ratio(a)	Bacharach Smoke No. Additive(b)
			Additive mg/Nm^3	Baseline mg/Nm^3		
	c. Evaluation Runs With Pure Compound Organic Additives					
39	Ethyl hexoic acid	0.03% by vol.	83.9	83.8	0.95	4
40	Naphthenic acid	0.05% by vol.	69.7	74.8	0.79	4
41	Ethyl alcohol	1.5% by vol.	83.1	98.5	0.94	4
42	Hexyl alcohol	1.5% by vol.	64.8	70.5	0.73	4
43	Toluene	0.2% by vol.	86.7	79.3	0.98	4
44	Toluene	0.2% by vol.	93.2	88.9	1.05	4
45	Diglyme	1.5% by vol.	89.8	104.5	1.01	3.5
		(Arithmetic mean for baseline runs (Runs 13-45)		88.6		

d. Evaluation Runs With Variable Boiler Load at Constant Air/Fuel Ratio

Run	Additive	Dosage	Firing Rate, lb/hr	Particulate Loading	
				Additive mg/Nm(3)	Baseline mg/Nm(3)
46	Barium naphthenate	51 ppm	98	55.1	121.6
47	ditto ditto	51 ppm	66	45.3	94.1
48	" "	51 ppm	54	41.5	86.1
49	" "	51 ppm	36	45.3	120.7

e. Evaluation Runs With Cyclic-Boiler Operation

Run	Additive	Dosage	Particulate Loading		
			Additive mg/Nm^3	Baseline mg/Nm^3	Additive/Baseline Ratio
50	Barium naphthenate	51 ppm	109.4	168.4	0.65

(a) The ratio of the particulate loading of the additive run to the arithmetic mean of the particulate loadings of the appropriate baseline runs.

(b) The Bacharach smoke number for the baseline run (12.8 percent CO_2) was 4.

TABLE 6. SUMMARY OF EVALUATION RUNS WITH TWO PERCENT SULFUR RESIDUAL OIL

Run	Additive	Additive Dosage	Particulate Loading Additive mg/Nm^3	Particulate Loading Baseline mg/Nm^3	Particulate Loading Ratio[(a)]	Bacharach Smoke No. Additive[(b)]
	(a) Evaluation Runs With Proprietary Additives					
51	CI-2 (Ethyl Corp)	53 ppm Mn	60.2	73.5	0.84	3
52	CI-2 (Ethyl Corp)	76 ppm Mn	59.6	73.5	0.83	3
53	CI-2 (Ethyl Corp)	27 ppm Mn	66.3	78.7	0.92	4
54	Ferrocene (Arapahoe)	27 ppm Fe	51.3	75.6	0.71	3.5
55	Watcon 130 (Industrial Chem.)	13 ppm Fe	53.7	80.9	0.75	3
56	Watcon 130 (Industrial Chem.)	27 ppm	42.7	80.0	0.59	2.5
57	Watcon 130 (Industrial Chem.)	20 ppm Fe	45.5	80.9	0.63	3
58	MC-7 Soluble (Apollo Chem.)	27 ppm Mn, 20 ppm Ba	50.6	74.5	0.70	3
59	MC-7 Soluble (Apollo Chem.)	27 ppm Mn, 20 ppm Ba	44.9	60.7	0.62	2.5
60	MC-7 Soluble (Apollo Chem.)	18 ppm Mn, 14 ppm Ba	51.2	74.5	0.71	3
61	Formula LSD (Commercial Chem.)	12 ppm Mn, 10 ppm Co, .02% by vol.	51.8	64.8	0.72	3.5
62	Rolfite 404 (Andrew Rolfe Chem. Co.)	30 ppm Mn	68.6	71.1	0.95	3.5
63	R-4000 (Triple E Products)	0.03% by vol. (no metal)	62.7	63.8	0.87	4
	(b) Evaluation Runs With Pure Compound Organo-Metallic Additives					
64	Barium hexoate	27 ppm Ba	50.6	72.3	0.70	3
65	Barium hexoate	18 ppm Ba	53.2	77.3	0.74	3
66	Barium hexoate	40 ppm Ba	47.8	68.3	0.66	3
67	Barium sulfonate	20 ppm Ba	52.0	70.9	0.72	3
68	Barium sulfonate	22 ppm Ba	49.7	78.1	0.69	3
69	Barium sulfonate	33 ppm Ba	48.1	78.1	0.67	2
70	Barium naphthenate	27 ppm Ba	56.9	71.2	0.79	1
71	Barium naphthenate	103 ppm Ba	44.7	66.9	0.62	1
72	Barium naphthenate	77 ppm Ba	45.5	66.9	0.63	1
73	Barium naphthenate	51 ppm Ba	41.7	65.7	0.58	1.5
74	Calcium naphthenate	27 ppm Ca	41.9	70.9	0.58	1
75	Calcium naphthenate	9 ppm Ca	50.0	72.4	0.69	3
76	Calcium naphthenate	54 ppm Ca	43.4	73.4	0.60	1.5
77	Iron naphthenate	27 ppm Fe	48.7	66.9	0.67	2.5
78	Iron pentacarbonyl	27 ppm Fe	46.6	66.9	0.65	3.5
79	Calcium and iron naphthenate	14 ppm Ca, 14 ppm Fe	43.3	76.7	0.60	2.5
80	Zinc naphthenate	27 ppm Zn	73.1	70.8	1.01	4
81	Zinc naphthenate	54 ppm Zn	85.0	73.4	1.18	3.5
	(c) Evaluation Runs With Pure Compound Organic Additives					
82	Naphthenic acid	0.1% by vol.	66.7	68.9	0.92	3.5
83	Hexoic acid	0.1% by vol.	74.1	68.9	1.03	4.0
		Arithmetic mean for baseline runs (Runs 51 to 83)		72		

(a) The ratio of the particulate loading of the additive run the particulate loadings of the appropriate baseline runs.

(b) The Bacharach smoke number for the baseline run (12.8 percent CO_2) was 4.

TABLE 6 (continued)

TABLE 6. (continued)

(d) Evaluation Runs at an Air/Fuel Equivalent to 14.2% CO_2

Run	Additive	Dosage	Particulate Loading Additive mg/Nm^3	Particulate Loading Baseline mg/Nm^3
84	Calcium naphthenate	27 ppm, Ca	62.3	144.2
85	Barium hexoate	40 ppm, Ba	73.8	144.2
86	Barium naphthenate	51 ppm, Ba	73.7	155.2

(e) Evaluation Runs With a Detuned Boiler

Run	Additive	Dosage	Particulate Loading Additive mg/Nm^3	Particulate Loading Baseline mg/Nm^3	Particulate Loading Additive/Baseline Ratio
87(b)	Barium naphthenate	51 ppm Ba	55.7	71.3	0.78
88(b)	Cobalt naphthenate	27 ppm Co	49.7	87.0	0.57
89(b)	CI-2 (Ethyl Corp)	27 ppm Mn	51.4	87	0.59
90(b)	MC-7 Soluble (Apollo)	35 ppm Ba, 14 ppm Mn	32.9	71.3	0.46

(f) Long-Term Evaluation Runs

Run	Additive	Dosage	CO_2 percent	Particulate Loading, mg/Nm^3	Bacharach Smoke No.
91	Barium naphthenate	51 ppm Ba	14.2	73.7	4
92(c)	Barium naphthenate	51 ppm Ba	12.8	39.1	2
93(c)	Calcium naphthenate	27 ppm Ca	12.8	35.9	1.0
94(c)	CI-2 (Ethyl Corp)	27 ppm Mn	12.8	40.9	2.5

(c) Second load of residual oil.

SECTION 8

INTERPRETATION OF RESULTS

Tables 4, 5, and 6 include the particulate loadings for both the daily baseline run and the additive run made that same day. The data were statistically treated to determine what level of variation in the particulate loading by additive utilization was statistically meaningful. The arithmetic mean of the particulate loading of the daily baseline runs was used as the standard for evaluating the effectiveness of additives in reducing particulate emissions. For the same oil, as discussed earlier, the ash loading for every baseline run should be nearly the same and, accordingly, any deviation in the baseline particulate loadings from day-to-day would have to be attributed to the deviations in the carbon portion of the particulate loading. Assuming that the variations in the particulate loadings for the daily baseline runs were the result of random instrument or measurement errors, the use of the arithmetic mean of the particulate loadings of all daily baseline runs minimizes the effect of these random variations on the additive evaluation. However, it may bias the results somewhat in that additives with high (or low) daily baseline particulate loadings (assuming these observed loadings are "real") appear less (or more effective than if the particulate loading of the additive run had been compared with the specific daily baseline loading. Regardless of which method of comparison is used, the overall conclusions would be similar.

DISTILLATE OIL EVALUATION RUNS

Figure 8 graphically shows that the use of additives can be detrimental in those systems that generate no appreciable quantities of carbon particulate. When firing distillate oil without an additive, analysis of the particulate catch indicated less than 1 percent carbon present for boiler operation with less than 8 percent excess air (14 percent CO_2). Accordingly, the addition into the oil of the metallic inert contained in the additive

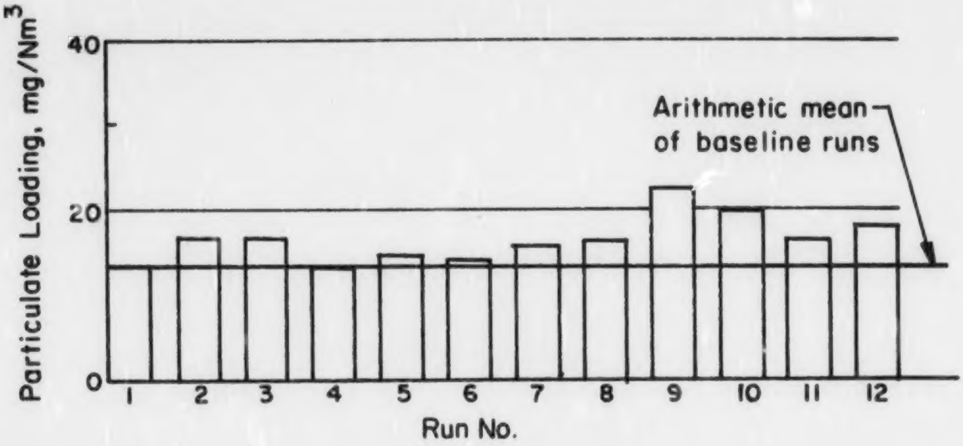

FIGURE 8. SUMMARY OF THE ADDITIVE EVALUATION RUNS WITH DISTILLATE OIL AT 80 PERCENT LOAD AND 14.0 PERCENT CO_2

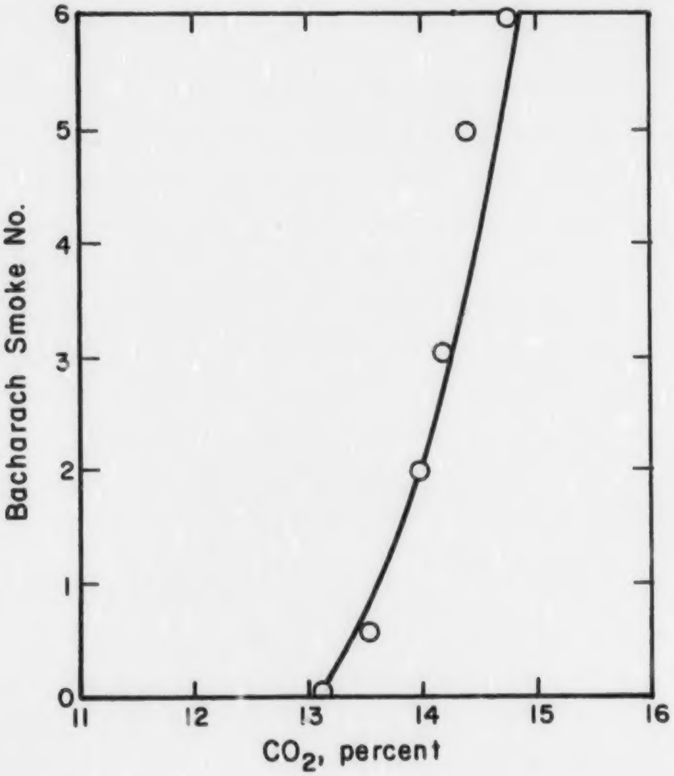

FIGURE 9. SMOKE VERSUS CO_2 LEVEL FOR REFERENCE DISTILLATE OIL

could only increase the particulate loading. Evaluation runs were not conducted at higher particulate loadings because the air/fuel ratio could not be controlled with sufficient accuracy to obtain reproducible particulate emission data. As shown in Figure 9, for CO_2 levels above 14 percent, a slight change in the air/fuel ratio would produce a significant change in particulate emission level.

It can be conjectured that the use of additives with distillate oil firing would allow boilers to be operated at lower excess levels (where appreciable carbon particulate would be generated without additives) and, thereby, increase efficiency. If it were possible to operate at these low excess air levels, sophisticated controls or manual attention would be required to control the air/fuel ratio precisely, as any slight change in boiler operation (e.g., fuel temperature, air temperature, etc.) could cause a drastic change in the excess air level and the emission of particulates, CO, and unburned hydrocarbons. Figure 9 illustrates this point for smoke. Only in the largest boilers would these controls be economically feasible, and the larger oil-fired boilers generally are fired with residual fuel oil.

RESIDUAL OIL EVALUATION RUNS

Additives were evaluated with two different residual oils, a 1-percent sulfur oil and a 2-percent sulfur oil. In general, the results of the evaluation runs with the two oils were similar. The difference in the baseline particulate loadings for the two oils (88.6 mg/Nm^3) for the 1-percent sulfur oil and 72.1 mg/Nm^3 for the 2-percent sulfur oil) is attributed to differences in physical and chemical properties of the fuels.

Statistical Significance

Figure 10 shows graphically the effectiveness of the proprietary additives and the organo-metallic and organic pure compound additives in reducing filterable particulate emissions from the combustion of the 1-percent sulfur residual oil fired continuously at 80 percent load and 12.8 percent CO_2. The arithmetic mean particulate emissions for the baseline runs, 89 mg/Nm^3, and the estimated ash component of the particulate loading are shown.

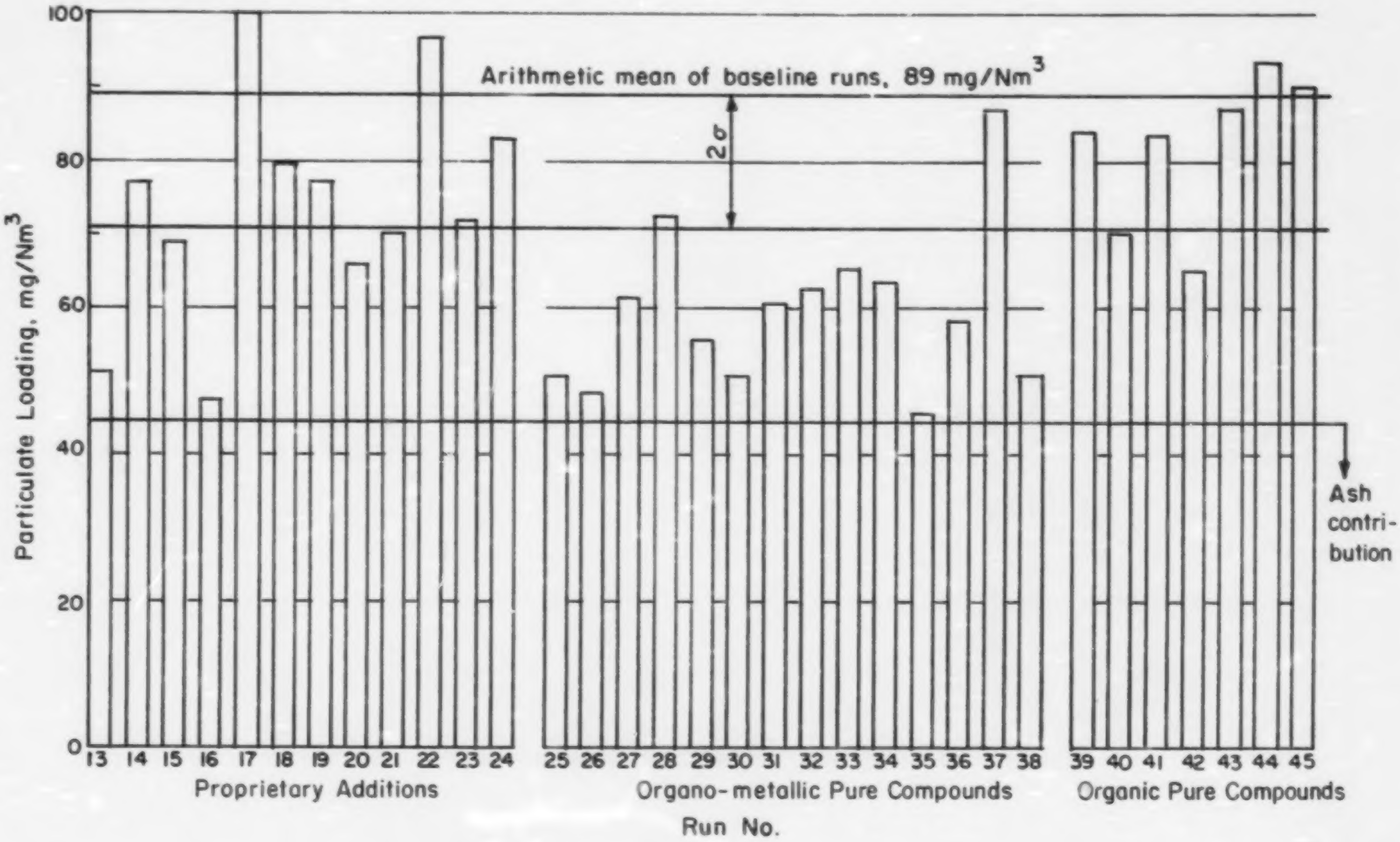

FIGURE 10. SUMMARY OF THE ADDITIVE EVALUATION RUNS WITH THE ONE PERCENT SULFUR RESIDUAL OIL AT 80 PERCENT LOAD AND 12.8 PERCENT CO_2

Also shown in Figure 11 is a line located at two standard deviations ($2\sigma = 18$ mg/Nm^3) below the baseline average. This standard deviation is based on the individual baseline measurements and is regarded as equally valid for the particulate measurements with additives. Although the use of two standard deviations strictly requires the assumption of normality to correspond to a 95 percent confidence level, it is used here in a broad sense to indicate a reasonably high, but unknown, confidence level. Additives producing particulate emission levels falling below this line (at 71 mg/Nm^3) are concluded to have been effective in reducing particulate emissions with a statistical significance (not due to chance) at this reasonably high confidence level. Additives producing particulate emission levels above 71 mg/Nm^3 but below 86 mg/Nm^3 (determined from the standard error of the mean of the baseline runs) suggest that these additives are effective, but that more experimental data are required to establish the level of statistical significance.

In addition, the measurements indicate that some additives are more effective in reducing particulate than others. However, by assuming that a standard deviation of 9 mg/Nm^3 also applies to the additive runs, a statistical treatment of the data would indicate that improvement with the various effective additives was not statistically different.

Likewise, Figure 11 graphically shows the effectiveness of proprietary, organo-metallic, and organic metallics in reducing particulate from the combustion of the 2-percent sulfur residual oil fired continuously at 80 percent load and 12.8 percent CO_2.

The arithmetic mean of these runs is 72 mg/Nm^3 while the standard deviation is only 5 mg/Nm^3. Again, the same statistical reasoning discussed previously applies to these runs.

Effect of Additive Type and Concentration

The data presented in Tables 5 and 6 and Figures 8 and 9 show that some additives containing metals substantially reduced particulate emissions. The additives that were effective contained certain alkaline-earth or transition

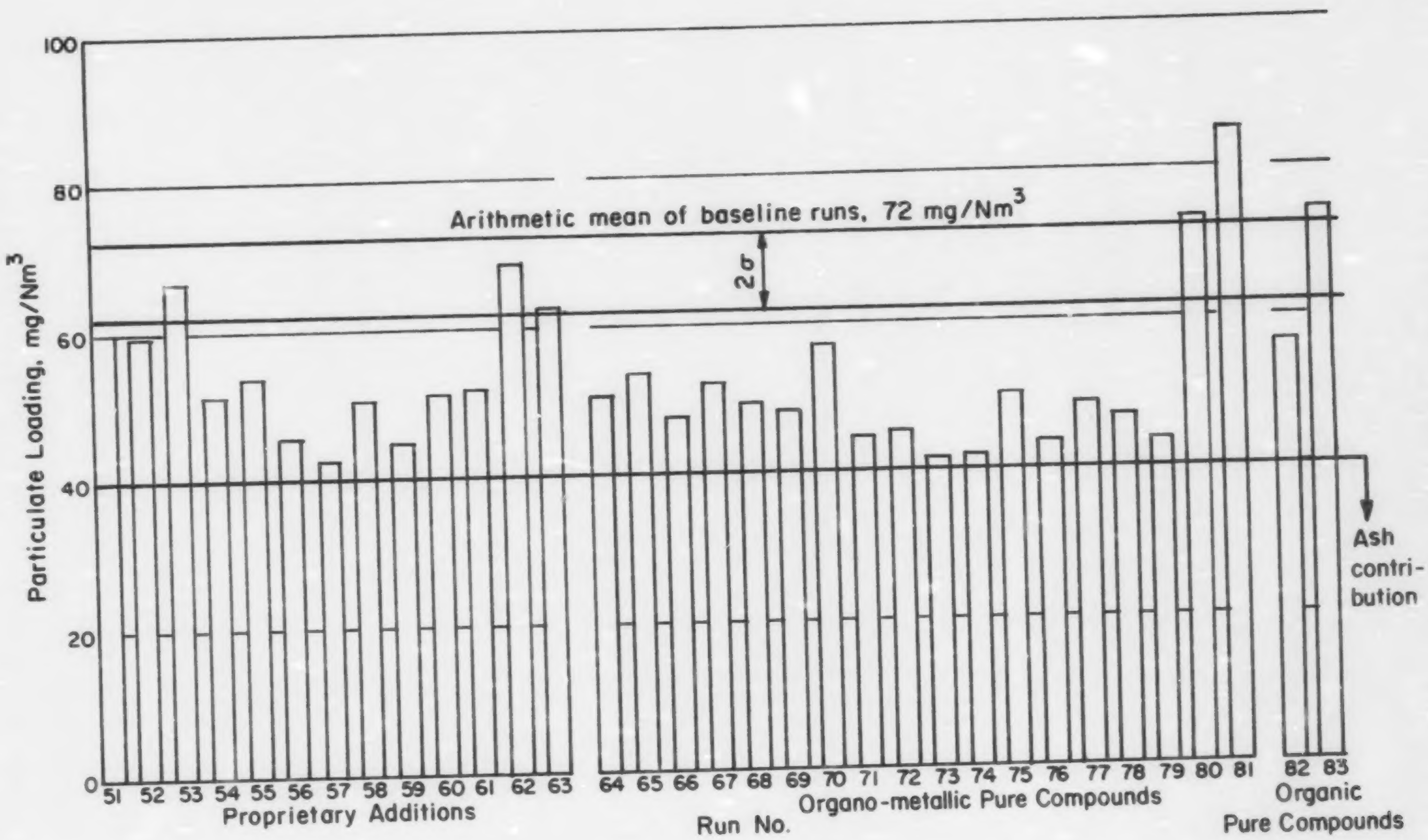

FIGURE 11. SUMMARY OF THE ADDITIVE EVALUATION RUNS WITH THE TWO PERCENT SULFUR RESIDUAL OIL AT 80 PERCENT LOAD AND 12.8 PERCENT CO_2

metals and were used in concentrations corresponding to the addition of between 20 ppm and 50 ppm of metal to the fuel oil. Proprietary additives of the organic type with some trace metals also were shown to be effective at concentrations that corresponded to the addition of at least 15 ppm of metal to the fuel oil. As in the case of the additive "Formula LSD", these concentrations were significantly higher than those recommended by the manufacturer.

In general, the organo-metallic compounds listed in Tables 5 and 6 were effective in reducing particulate except for an additive in the subclass cyclopentadienes (CI-2) and zinc naphthenate. The proprietary additive CI-2 (represented by Runs 17, 18, 51, and 53), although observed to be effective in reducing particulate from a residential oil burner firing distillate oil (1), proved only marginally effective in the 50-bhp (500 kW boiler firing residual oil; its ineffectiveness might be attributed to the type of bonding structure of this compound, although Ferrocene (Run 54), another type of metallic cyclopentadiene, proved effective in reducing carbon particulate. The data indicate that the most effective additive constituents are compounds of the alkaline-earth metals (barium and calcium) and the transition metals (manganese, iron, and cobalt). Zinc, an element just beyond the above transition metals, was found to be an ineffective additive.

The use and effectiveness of the "effective" additives at higher concentrations might be expected to produce a greater reduction in emissions. However, it was observed that, even though carbon burnout can be further promoted at higher concentrations, the net reduction in particulate is not substantial because of the additional particulate generated by the metallic inert contained in the additive.

Some of the pure organic additives appeared effective in reducing particulate emissions. However, these additives had to be used at impractically high concentrations to be marginally effective and, therefore, could not be considered as a viable method of controlling particulate emissions.

The organic acids, naphthenic and hexoic (Runs 82 and 83) were only evaluated to determine if the organic carrier of the metal in the organo-metallic additives had any effect on particulate reduction. Obviously they did not.

Effect of Additives on Carbon Particulate

For the baseline operating condition of 80 percent load at 12.8 percent CO_2, the carbon content of the filterable particulate from the majority of runs with both residual oils was measured as between 40 and 50 percent (with the remaining portion being the ash component associated with the inerts of the fuel oil). Accordingly, because combustion additives are intended to promote more complete burnout of carbon, they can only reduce particulate loadings by up to 50 percent--unless the use of additives caused a larger portion of the particulate to remain within the combustion system. This would probably be undesirable, as it would cause fouling of heat transfer surfaces.

From Figures 10 and 11, it can be seen that the most effective additives reduced particulate loading levels to values comparable with particulate generated by the ash in the fuel. This reduction represents about a 50 percent reduction in particulate emissions and the nearly total elimination of carbon particulate emissions.

Variable Load Runs. This observation that particulate loading can be reduced by about 50 percent is further verified by the results of Runs 25, 26, 46, 47, 48, and 49 in which the boiler was fired at five boiler loads. Figure 12 shows the particulate loading generated by the boiler operated at each of five loads with and without barium naphthenate as the additive. For the baseline runs, particulate loadings were higher at the extremes of the load range. However, with the use of barium naphthenate, particulate loadings were reduced to approximately the same level, regardless of load. The average particulate loading for these additive runs was about 10 percent higher than the anticipated ash level from firing the referenced fuel alone--this can be attributed to the increase in metallic inert of the oil by addition of the barium naphthenate. Analysis of the particulate catch obtained from these additive runs showed that over 80 percent of the particulate was ash (or less than 20 percent of the particulate was carbon).

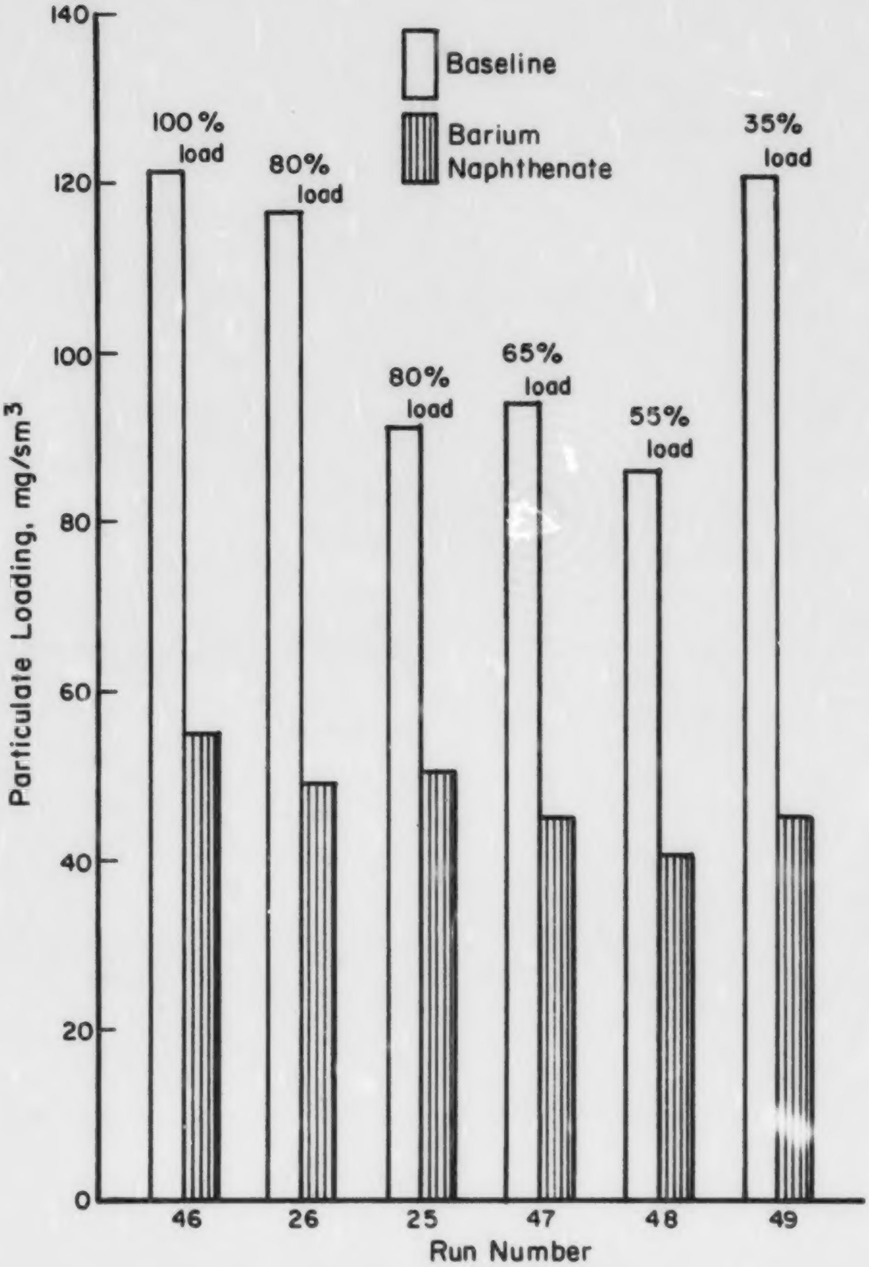

FIGURE 12. THE EFFECTIVENESS OF BARIUM NAPHTHENATE IN REDUCING PARTICULATE AT VARIABLE BOILER LOAD FOR CONSTANT AIR/FUEL RATIO WITH RESIDUAL OIL

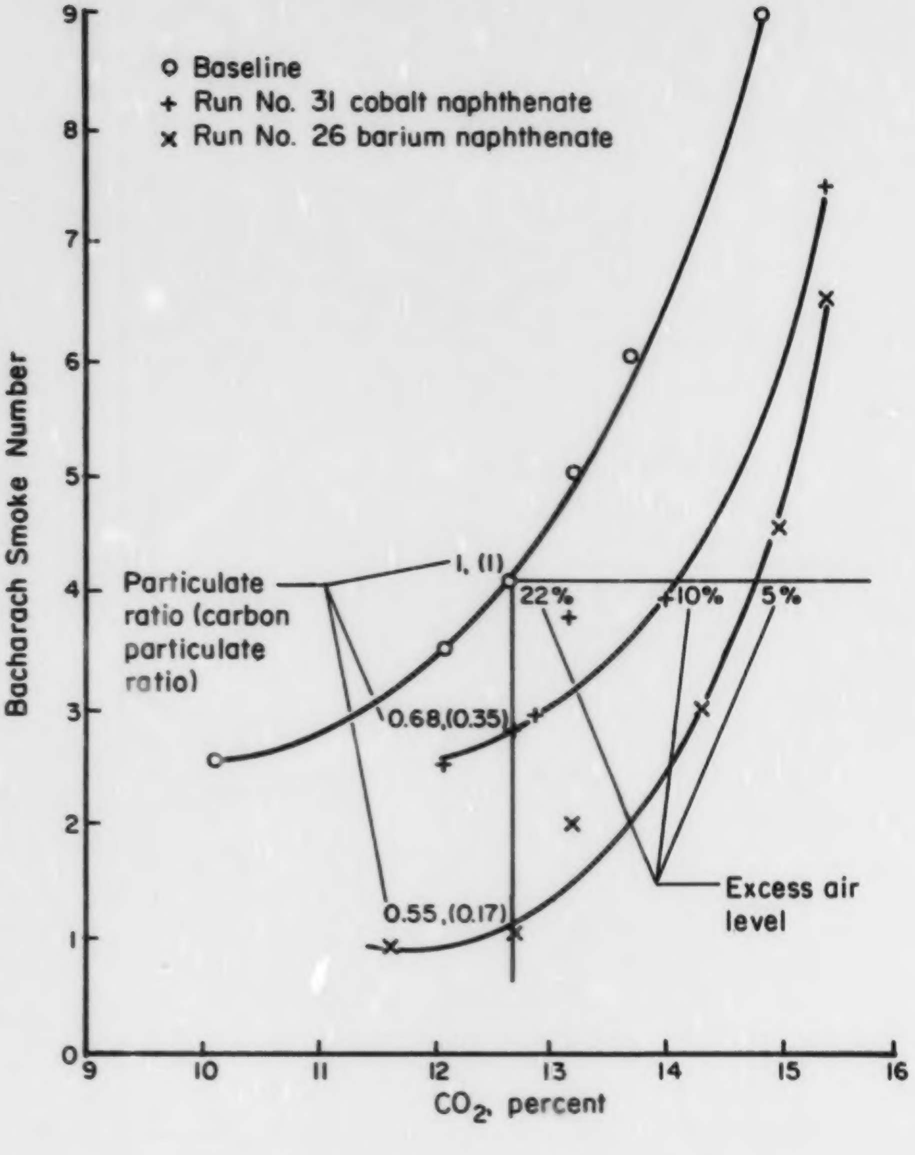

FIGURE 13. SMOKE VERSUS CO$_2$ LEVEL FOR THE RESIDUAL OIL AND SELECTED ADDITIVES. The numbers apply to the intersection of the curves with the coordinate lines.

Effect of Additives on Smoke

As a measure of the effectiveness of additives in reducing particulate emissions over a range of air/fuel ratios, Bacharach smoke measurements were made at about 6 excess air levels for every daily baseline run and every additive run to enable plots as in Figure 13. This figure shows the effect of cobalt naphthenate (Run 31) and barium naphthenate (Run 26) on smoke emissions. In general, the relation between Bacharach smoke and CO_2 for the daily baseline runs (as shown by the curve in Figure 13) remained constant from day-to-day--as would be expected from the small variations in particulate loadings of these runs. Accordingly, the effectiveness of the additive could be evaluated semiquantitatively by comparing the smoke characteristic curves with and without the additive. The differences in smoke levels of these curves could be related to the differences in both total and carbon particulate loadings at some CO_2 level. For example, at 12.8 percent CO_2, examination of the data from Figure 13, Table 5, and the analyses of the filter catches of Runs 26 and 31 for carbon, indicates the following

	Reduction in Bacharach Smoke No. from 4 to	Particulate Loading Ratio	
		Total Particulate	Carbon Particulate
Run 26, Barium naphthenate	1.0	0.55	0.17
Run 31, Cobalt naphthenate	2.5	0.68	0.35 .

Thus, these additives were effective in reducing both smoke and carbon particulate, and the additive (barium naphthenate) that was most effective in reducing smoke emissions also was most effective in reducing particulate emissions.

Effect of Additives on Carbon Particulate at Higher Loadings

In Runs 84, 85, and 86, additives were evaluated at a boiler operating condition of 14.2 percent CO_2, an operating point at which approximately three times the carbon particulate is generated as at 12.8 percent CO_2. (This factor of three was determined by carbon analysis of the filter catches for the baseline runs at 14.2 percent CO_2 and 12.8 percent CO_2.) A comparison of the carbon analysis of the filter catches of these runs with those for the same additives and additive concentrations (Runs 64, 73, and 74) indicates that, at the higher particulate loading (presumably due to increased carbon emission), additives removed a lower percentage of the carbon particulate but a larger total amount. Table 7 summarizes these results.

TABLE 7. ANALYSIS OF FILTER CATCHES FOR SELECTED ADDITIVES AT BOILER OPERATING CONDITION OF 12.8 PERCENT CO_2 AND 14.2 PERCENT CO_2.

Run	Carbon, mg		Carbon for Baseline Run Minus Carbon for Additive Run, mg		Carbon Reduction With Additive, percent	
CO_2, %	12.8	14.2	12.8	14.2	12.8	14.2
Baseline	45	125	--	--	--	--
64, 85 (barium hexoate)	6	35	39	90	87	72
73, 86 (barium naphthenate)	7	35	38	90	85	72
74, 84 (calcium naphthenate)	3	21	42	104	93	83

These results are consistent with the model that proposes that the increased carbon particulate loading at 14.2 percent CO_2 is due to an increase in particle size (rather than an increase in number of particles), and that the action of the additive in destroying the carbon particles is surface limited. Accordingly, as the carbon particles increase in size there is more surface to react with the additive and thus, a larger amount of carbon can be destroyed. However, as the particle size increases, the surface-to-mass ratio decreases restricting the reaction of the additive on the total mass of carbon.

Effect of Additives With a Detuned Boiler

The boiler was "detuned" following the above reported additive runs to simulate a boiler in poor operating condition by (1) replacing the standard 20 gal/hr (76 ℓ/hr) nozzle with a 10 gal/hr (38 ℓ/hr) nozzle, while maintaining firing rate, (2) decreasing oil preheat temperature from 170 F to 135 F (77 C to 57 C), and (3) bleeding off a portion of the atomizing air. This third change had the most dramatic effect in that the fuel spray would impinge on the wall and produce a locally smoky fuel-rich flame. Although the overall air/fuel ratio could be controlled to maintain a constant CO_2 level of 12.8 percent, smoke levels for the baseline runs at this air/fuel ratio would vary from Bacharach smoke of 3 to 7. In addition, the smoke characteristic curves could not be reproduced with any high degree of accuracy.

The use of the additives in the "detuned" boiler (Runs 87, 88, 89, and 90) did not improve the reproducibility of the smoke data over the range of air/fuel ratios of interest (9 to 14 percent CO_2), although the additives decreased the smoke levels somewhat. These additives appeared to be more effective in reducing smoke from a "tuned" boiler than a "detuned" boiler. However, the relative reduction in relative particulate emission levels was about the same for either a tuned or detuned boiler. Apparently, the additives were not effective in destroying or inhibiting the formation of soot or smoke produced from the fuel distilled off the combustion chamber walls.

Effect of Additives in Cyclic Operation

To obtain a measure of the effectiveness of additives in a more normal operating mode for small boilers, an evaluation run (Run 50) was conducted while the boiler was operated on a cycle of 15 minutes on and 5 minutes off at 80 percent load and 12.8 percent CO_2. (This would not be a typical operating cycle for most larger commercial boilers and nearly all industrial boilers. To meet a varying load, the firing rate for these boilers is modulated so that there is continuous combustion.) If the assumption is made that the ash component of the particulate emission is the same for cyclic operation as it is for steady-state operation, the additive reduced carbon particulate by only 50 percent in cyclic operation in comparison to over 80 percent for steady-state operation. During this mode of operation, the character of the particulate (such as unburned vaporized fuel oil or larger particle size) could be different than during steady-state combustion. The additive may not be as effective in reducing the quantity of this altered particulate.

While these results are illustrative, additional information is needed on the effect of additives under different conditions of cyclic operation for small commercial boilers.

Effect of Additives on POM

Table 8 summarizes the polycyclic organic matter (POM) data that includes both the steady-state and cyclic runs. Sampling and analysis for POM were conducted during a limited number of additive runs that are indicated by the suffix "a" in Table 8. The data in Table 8 include both the total POM and species quantification for over 15 compounds, the majority of which are listed as potentially carcinogenic by the National Academy of Science (12). The "stars" indicate the relative levels of potential carcinogenicity, with no stars being noncarcinogenic while the 4 stars indicate the highest level.

Steady-State Runs. Table 9 includes a comparison of the total POM loadings with carbon particulate loadings and Bacharach smoke levels for the runs listed. From Table 9, and as discussed previously, certain additives are effective in reducing carbon particulate for the residual oil runs; however, the effect of additives on POM emission levels is somewhat inconclusive because of the large amount of scatter in the data points and the limited number of POM baseline data. From Figure 14, a plot of particulate and POM loadings as a function of CO_2 (and, thus, excess air) generated during the residual oil checkout runs, the scatter of data in Table 9 is not unexpected when considering that a small decrease in excess air can drastically increase the POM emission level due to the sharp change in the slope of the POM curve at 12.8 percent--where the additive evaluation runs were made. In addition, because the concentration of POM in the liquid fuel is 20,000 to 100,000 times greater than the concentration measured in the stack gas, any emission of unburned fuel can have a great effect on the POM levels measured in the stack. Thus, it is possible that subtle changes in the combustion process (that cannot be detected by gross analysis of stack gas composition) may have a significant effect on POM emissions. Such factors would tend to mask an additive effect, especially considering that for most runs POM loadings were observed to be less than 10 $\mu g/Nm^3$ for continuous steady-state operation and that these levels approach the threshhold level of measurement.

TABLE 8. POM QUANTIFICATION
(The suffix "a" denotes evaluation run with an additive.)

Component	NAS (13) Notation	Run 1		Run 1a		Run 2a		Run 3a	
		ng	µg/Nm^3	ng	µg/Nm^3	ng	µg/Nm^3	ng	µg/Nm^3
Anthracene/Phenanthrene		4,360	2.4	2,890	1.4	1,160	0.1	5,140	0.6
Methyl anthracenes		2,570	1.4	300	0.1	-	-	2,560	0.3
Fluoranthene		1,130	0.6	970	0.5	180	0.0	890	0.1
Pyrene		330	0.2	490	0.2	150	0.0	360	0.1
Methyl Pyrene/Fluoranthene									
Benzo(c)phenanthrene	***	-	-	30	0.0	-	-	-	-
Chrysene/Benz(a)anthracene	*	240	0.1	110	0.1	200	0.0	220	0.0
Methyl chrysenes	*	-	-	-	-	-	-	-	-
7,12-Dimethylbenz(a)anthracene	****	-	-	-	-	-	-	-	-
Benzo(k and b)fluoranthenes	**	-	-	-	-	-	-	120	0.0
Benzo(j)fluoranthene	**	-	-	-	-	-	-	-	-
Benz(a and e)pyrenes	***	-	-	-	-	-	-	-	-
Perylene		-	-	-	-	-	-	-	-
3-Methylcholanthrene	****	-	-	-	-	-	-	-	-
Indeno(1,2,3,-cd)pyrene	*	-	-	-	-	-	-	-	-
Benzo(ghi)perylene		-	-	-	-	-	-	-	-
Dibenzo(a,h) anthracene	***	-	-	-	-	-	-	-	-
Dibenzo(c,g)carbazole	***	-	-	-	-	-	-	-	-
Dibenz(ai and ah)pyrenes	***	-	-	-	-	-	-	-	-
TOTAL		8,630	4.7	4,790	2.3	1,690	0.1	9,290	1.1

(continued)

(The suffix "a" denotes evaluation
run with an additive.)

Component	NAS Notation	Run 4a		Run 5a		Run 11a		Run 13a	
		ng	µg/Nm^3	ng	µg/Nm^3	ng	µg/Nm^3	ng	µg/Nm^3
Anthracene/Phenanthrene		1,740	1.5	7,050	0.8	20,440	11.1	1,120	0.7
Methyl anthracenes		480	0.4	1,890	0.2	23,370	12.7	210	0.1
Fluoranthene		320	0.3	7,390	0.8	870	0.5	-	-
Pyrene		70	0.1	5,500	0.6	220	0.1	-	-
Methyl Pyrene/Fluoranthene		-	-	3,960	0.4	-	-	-	-
Benzo(c)phenanthrene	***	-	-	820	0.1	70	0.1	-	-
Chrysene/Benz(a)anthracene	*	190	0.2	18,430	2.0	220	0.1	-	-
Methyl chrysenes	*	-	-	1,660	0.2	-	-	-	-
7,12-Dimethylbenz(a)anthracene	****	-	-	18,990	2.1	-	-	-	-
Benzo(k and b)fluoranthenes	**	310	0.3	-	-	-	-	-	-
Benzo(j)fluoranthene	**	-	-	-	-	-	-	-	-
Benz(a and e)pyrenes	***	-	-	6,480	0.7	-	-	-	-
Perylene		130	0.1	40	0.0	-	-	-	-
3-Methylcholanthrene	****	-	-	-	-	-	-	-	-
Indeno(1,2,3,-cd)pyrene	*	-	-	1,420	0.2	-	-	-	-
Benzo(ghi)perylene		-	-	1,300	0.2	-	-	-	-
Dibenzo(a,h) anthracere	***	-	-	-	-	-	-	-	-
Dibenzo(c,g)carbazole	***	-	-	-	-	-	-	-	-
Dibenz(ai and ah)pyrenes	***	-	-	-	-	-	-	-	-
TOTAL		3,240	2.9	74,930	8.3	45,190	24.6	1,330	0.8

TABLE 8 (continued)

(The suffix "a" denotes evaluation
run with an additive.)

Component	NAS Notation	Run 14a		Run 15a		Run 16a		Run 17a	
		ng	µg/Nm^3	ng	µg/Nm^3	ng	µg/Nm^3	ng	µg/Nm^3
Anthracene/Phenanthrene		2,720	1.7	2,400	1.5	1,860	1.2	3,950	2.6
Methyl anthracenes		450	0.3	940	0.6	3,350	2.2	820	0.6
Fluoranthene		600	0.4	1,160	0.7	530	0.3	860	0.6
Pyrene		410	0.3	280	0.2	250	0.2	510	0.3
Methyl Pyrene/Fluoranthene									
Benzo(c)phenanthrene	***	20	0.0	-	-	-	-	-	-
Chrysene/Benz(a)anthracene	*	30	0.0	300	0.2	30	0.0	80	0.5
Methyl chrysenes	*	-	-	-	-	-	-	-	-
7,12-Dimethylbenz(a)anthracene	****	-	-	-	-	-	-	-	-
Benzo(k and b)fluoranthenes	**	40	0.0	-	-	-	-	10	0.0
Benzo(j)fluoranthene	**	-	-	-	-	-	-	-	-
Benz(a and e)pyrenes	***	-	-	-	-	-	-	-	-
Perylene		-	-	-	-	-	-	-	-
3-Methylcholanthrene	****	-	-	-	-	-	-	-	-
Indeno(1,2,3,-cd)pyrene	*	-	-	-	-	-	-	-	-
Benzo(ghi)perylene		-	-	-	-	-	-	-	-
Dibenzo(a,h) anthracene	***	-	-	-	-	-	-	-	-
Dibenzo(c,g)carbazole	***	-	-	-	-	-	-	-	-
Dibenz(ai and ah)pyrenes	***	-	-	-	-	-	-	-	-
TOTAL		4,270	2.7	5,080	3.2	6,020	3.9	6,230	4.6

TABLE 8 (continued)

(The suffix "a" denotes evaluation
run with an additive.)

Component	NAS Notation	Run 19a		Run 20		Run 20a		Run 25a	
		ng	µg/Nm^3	ng	µg/Nm^3	ng	µg/Nm^3	ng	µg/Nm^3
Anthracene/Phenanthrene		1,340	0.7	2,190	1.3	1,030	0.6	1,000	0.6
Methyl anthracenes		360	0.2	600	0.4	500	0.3	160	0.1
Fluoranthene		310	0.2	690	0.4	350	0.2	310	0.2
Pyrene		160	0.8	270	0.2	340	0.2	120	0.1
Methyl Pyrene/Fluoranthene		-	-	-	-	-	-	-	-
Benzo(c)phenanthrene	***	-	-	-	-	-	-	-	-
Chrysene/Benz(a)anthracene	*	-	-	350	0.2	260	0.2	120	0.1
Methyl chrysenes	*	-	-	-	-	-	-	-	-
7,12-Dimethylbenz(a)anthracene	****	-	-	-	-	-	-	-	-
Benzo(k and b)fluoranthenes	**	-	-	-	-	-	-	-	-
Benzo(j)fluoranthene	**	270	0.1	-	-	-	-	-	-
Benz(a and e)pyrenes	***	-	-	-	-	-	-	-	-
Perylene		-	-	-	-	-	-	-	-
3-Methylcholanthrene	****	-	-	-	-	-	-	-	-
Indeno(1,2,3,-cd)pyrene	*	-	-	-	-	-	-	-	-
Benzo(ghi)perylene		-	-	-	-	-	-	-	-
Dibenzo(a,h) anthracene	***	-	-	-	-	-	-	-	-
Dibenzo(c,g)carbazole	***	-	-	-	-	-	-	-	-
Dibenz(ai and ah)pyrenes	***	-	-	-	-	-	-	-	-
TOTAL		2,440	2.0	4,100	2.5	2,480	1.5	1,710	1.1

TABLE 8. (continued)

(The suffix "a" denotes evaluation
run with an additive.)

Component	NAS Notation	Run 31a		Run 46		Run 47		Run 48	
		ng	$\mu g/Nm^3$	ng	$\mu g/Nm^3$	ng	$\mu g/Nm^3$	ng	$\mu g/Nm^3$
Anthracene/Phenanthrene		480	0.3	1,570	1.1	9,510	8.5	4,780	3.0
Methyl anthracenes		840	0.6	-	-	-	-	-	-
Fluoranthene		-	-	790	0.6	15,800	14.1	4,350	2.7
Pyrene		370	0.3	380	0.3	210	0.2	150	0.1
Methyl Pyrene/Fluoranthene		-	-	-	-	-	-	90	0.1
Benzo(c)phenanthrene	***	-	-	-	-	-	-	-	-
Chrysene/Benz(a)anthracene	*	-	-	70	0.1	140	0.1	120	0.1
Methyl chrysenes	*	-	-	-	-	-	-	-	-
7,12-Dimethylbenz(a)anthracene	****	-	-	-	-	-	-	-	-
Benzo(k and b)fluoranthenes	**	70	0.1	-	-	-	-	-	-
Benzo(j)fluoranthene	**	-	-	-	-	20	0.0	20	0.0
Benz(a and e)pyrenes	***	-	-	-	-	-	-	-	-
Perylene		-	-	-	-	-	-	30	0.0
3-Methylcholanthrene	****	-	-	-	-	-	-	-	-
Indeno(1,2,3,-cd)pyrene	*	-	-	130	0.1	-	-	-	-
Benzo(ghi)perylene		-	-	410	0.3	-	-	-	-
Dibenzo(a,h) anthracene	***	-	-	-	-	-	-	-	-
Dibenzo(c,g)carbazole	***	-	-	-	-	-	-	-	-
Dibenz(ai and ah)pyrenes	***	-	-	-	-	-	-	-	-
TOTAL		1,760	1.3	3,350	2.5	25,680	22.9	9,540	6.0

TABLE 8. (continued)

Table 8 (continued)

(The suffix "a" denotes evaluation run with an additive.)

Component	NAS Notation	Run 49		Run 50		Run 50a	
		ng	μg/Nm^3	ng	μg/Nm^3	ng	μg/Nm^3
Anthracene/Phenanthrene		1,840	1.4	212,500	148.6	32,000	23.0
Methyl anthracenes		-	-	650,000	454.5	48,700	35.0
Fluoranthene		1,030	0.8	23,700	16.6	5,800	4.2
Pyrene		160	0.1	60,400	42.2	9,200	6.6
Methyl Pyrene/Fluoranthene		-	-	282,000	197.2	22,400	16.1
Benzo(c)phenanthrene	***	-	-	10,100	7.1	6,800	4.9
Chrysene/Benz(a)anthracene	*	20	0.0	-	-	9,900	7.1
Methyl chrysenes	*	-	-	35,500	24.8	28,500	20.5
7,12-Dimethylbenz(a)anthracene	****	-	-	-	-	-	-
Benzo(k and b)fluoranthenes	**	-	-	7,600	5.3	4,000	2.9
Benzo(j)fluoranthene	**	-	-	-	-	-	-
Benz(a and e)pyrenes	***	-	-	17,800	12.4	4,600	3.3
Perylene		-	-	-	-	-	-
3-Methylcholanthrene	****	-	-	-	-	-	-
Indeno(1,2,3,-cd)pyrene	*	-	-	21,900	15.3	-	-
Benzo(ghi)perylene		-	-	-	-	-	-
Dibenzo(a,h) anthracene	***	-	-	-	-	-	-
Dibenzo(c,g)carbazole	***	-	-	-	-	-	-
Dibenz(ai and ah)pyrenes	***	-	-	-	-	-	-
TOTAL		3,050	2.3	1,321,500	924.0	171,900	123.6

TABLE 9. COMPARISON OF POM LOADING WITH PARTICULATE LOADING AND SMOKE LEVEL

Run No.	Additive	Oil Type	Boiler Load % Full-Load	CO_2 %	POM Loading µg/nm^3	Particulate Loading Total mg/nm^3	Particulate Loading Carbon mg/nm^3	Bacharach Smoke Level
1	No additive	Distillate	80	14.0	4.7	13.6	≈ 0	2
1	CI-2 (Ethyl Corp.)	Distillate	80	14.0	2.3	14.4	≈ 0	2
2	MC-7 Soluble (Apollo Chem.)	Distillate	80	14.0	0.2	16.9	≈ 0	1.5
3	Formda LSD (Commercial Chem.)	Distillate	80	14.0	1.1	16.7	≈ 0	2
4	Rolfite 404 (Andrew Rolfe)	Distillate	80	14.0	2.9	16.5	≈ 0	2
5	PD 1654 (Arapohoe Chem.)	Distillate	80	14.0	8.3	14.5	≈ 0	1.5
11	Cobalt napthenate	Distillate	80	14.0	24.5	16.0	≈ 0	2
13	MC-7 Soluble (Apollo Chem.)	Residual (1% S)	80	12.8	0.8	51.1	7	3
14	Formite LSD (Commercial Chem.)	Residual (1% S)	80	12.8	2.7	77.0	33	3
15	Formite LSD (Commercial Chem.)	Residual (1% S)	80	12.8	3.1	68.9	25	3
16	Improsoot (Commercial Chem.)	Residual (1% S)	80	12.8	3.9	47.6	4	3
17	CI-2 (Ethyl Corp.)	Residual (1% S)	80	14.0	4.1	79.5	36	3.5
19	PD-1654 (Arapahoe)	Residual (1% S)	80	12.8	1.3	77.1	33	3
20	No additive	Residual (1% S)	80	12.8	2.5	87.2	43	4
20	Watcon 130 (Industrial Chem.)	Residual (1% S)	80	12.8	1.5	66.1	22	3
25	Barium naphthenate	Residual (1% S)	80	12.8	1.1	50.5	6	2
31	Cobalt naphthenate	Residual (1% S)	80	12.8	1.3	60.5	16	3
46	No additive	Residual (1% S)	100	12.8	2.5	121.6	78	4
47	No additive	Residual (1% S)	65	12.8	22.9	94.1	50	4
48	No additive	Residual (1% S)	55	12.8	6.0	86.1	42	4
49	No additive	Residual (1% S)	35	12.8	2.3	120.7	77	4
50	No additive	Residual (1% S)			924	168.4	124	-
50a	Barium napthenathenate	Residual (1% S)	80	12.8	124	109.4	65	-

However, from Figure 14 there appears to be a direct relation between particulate and POM emission levels suggesting that additives effective in reducing particulate emissions may also be effective in reducing POM emissions. Figure 15, a plot of POM loading versus particulate loading for Runs 13, 14, 15, 16, 17, 19, and 20 tend to further support this relation. Additional data, however, are required to determine the statistical significance of the effect of additives on POM.

Cyclic Runs. POM measurements were also made during the cyclic operation of the boiler in Run 50. Although this size boiler would not be operated in an on-off cycle, but rather modulated to meet load, it was felt that some useful data could be obtained by operating the boiler over a cycle of 15 minutes on and 5 minutes off. As noted in Table 5 for Run 50, particulate loadings increased by a factor of about two for both the baseline and the barium naphthenate additive runs. However, POM levels for the baseline run increased by over two orders of magnitude (924 $\mu g/Nm^3$), although the POM emissions still were much higher than for steady-state runs. The high levels of POM emissions observed during cyclic operation of the boiler could be attributed to several factors associated with the generation and formation of POM, including transients in atomization and ignition. It is believed that POM is generated in the 1000 F (540 C) to 1500 F (810 C) temperature range and that this temperature range occurs more frequently, or for a longer duration, in transient combustion than in continuous steady-state combustion. In addition because the POM concentration is higher in the fuel than in the stack gases, any unburned or partially burned fuel which enters the exhaust during startup and shutdown would increase POM emissions.

Effect of Additives on Particle Size

Particle-size measurements of particulate emissions were made using an Andersen cascade impactor for the baseline condition (no additive) and for two additives. These runs were conducted in the "tuned" boiler firing the 2 percent sulfur residual oil at the reference condition of 12.8 percent CO_2 at an 80 percent boiler load.

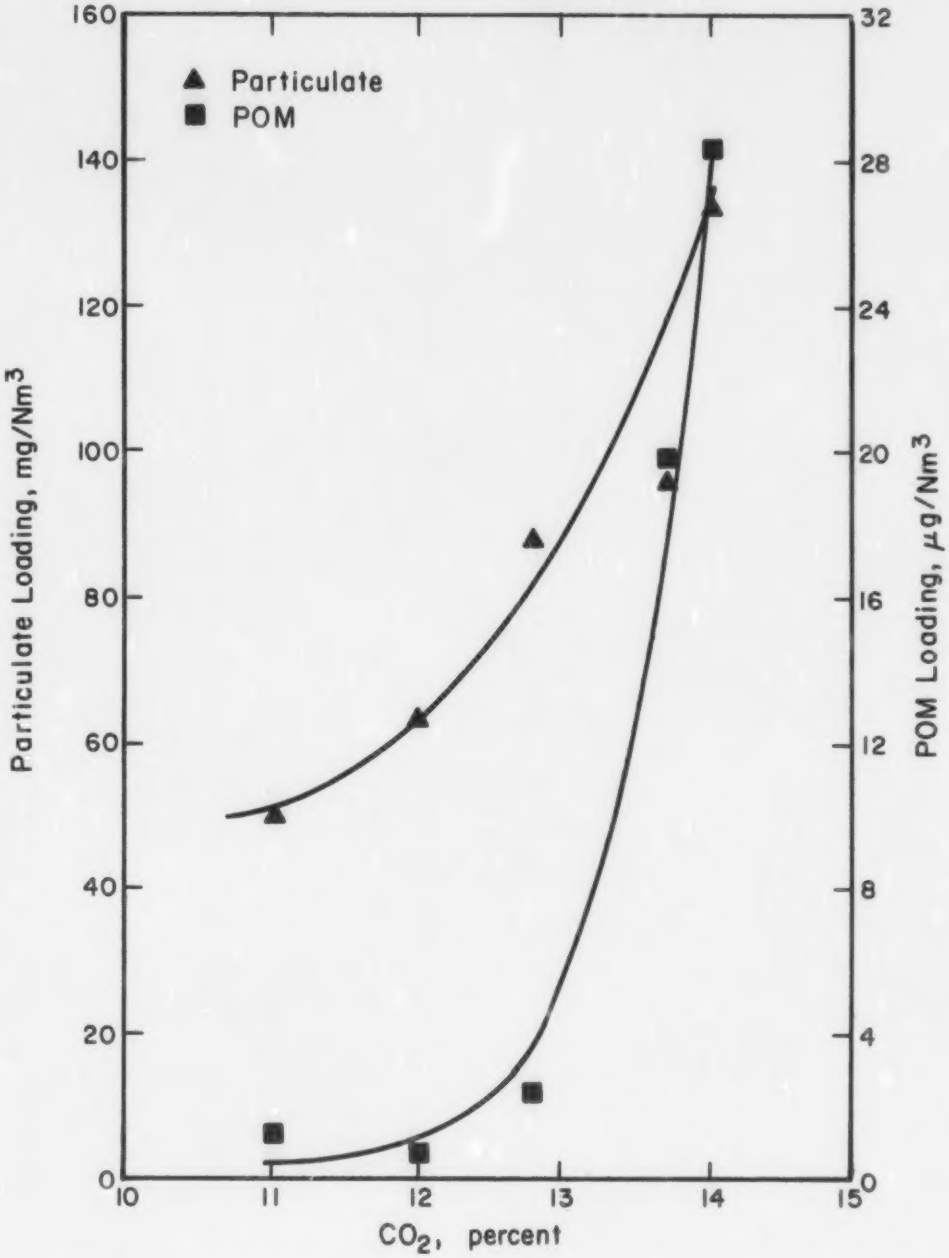

FIGURE 14. POM AND PARTICULATE LOADING AS A FUNCTION OF CO_2 FOR THE 1 PERCENT SULFUR RESIDUAL OIL

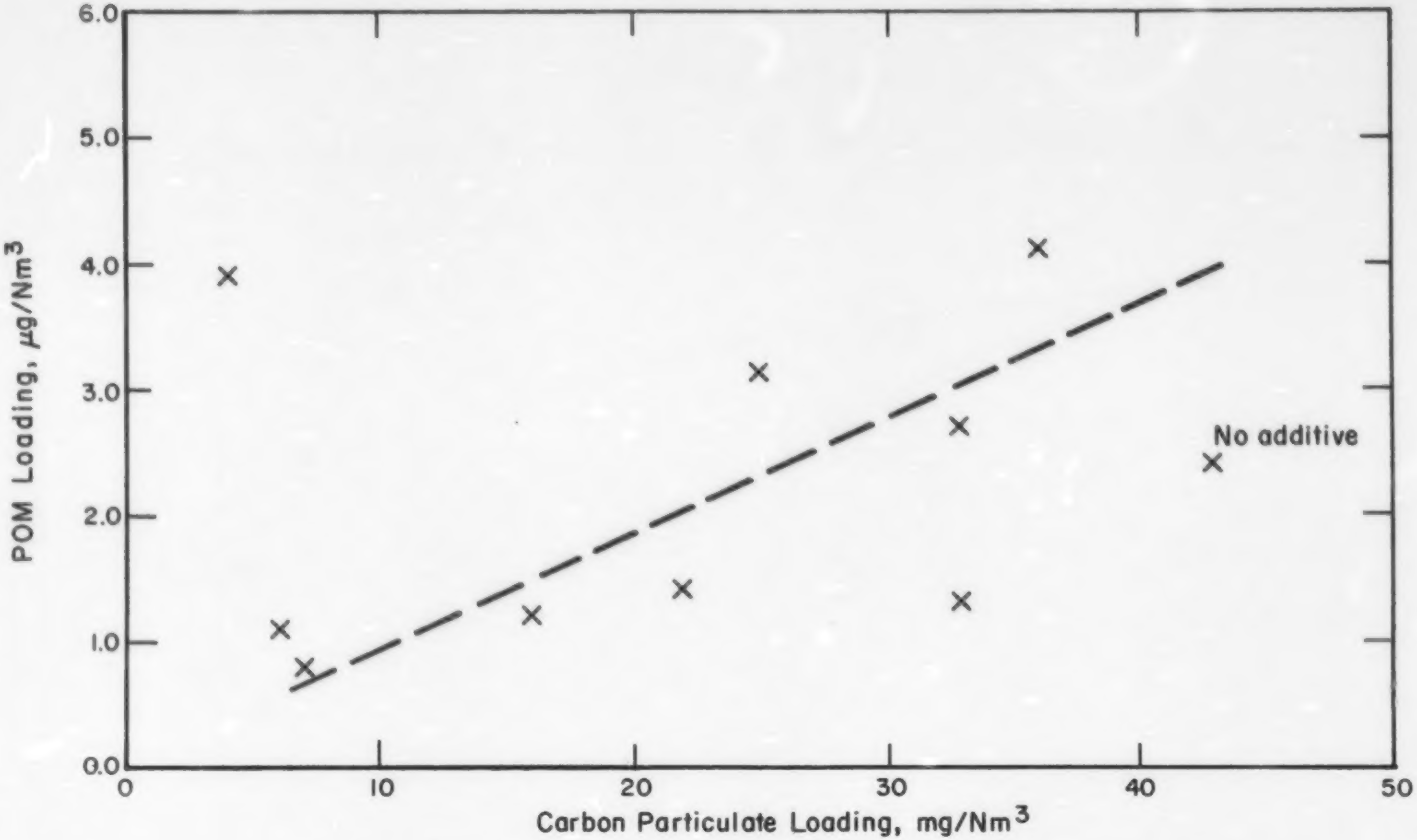

FIGURE 15. POM LOADING VERSUS PARTICULATE LOADING FOR RESIDUAL OIL AT 12.8 PERCENT CO_2 AND 80 PERCENT LOAD

Figure 16 shows the particle-size distribution of these runs plotted on log probability paper. For the conditions examined, both the barium naphthenate (51 ppm) and the Ethyl CI-2 (27 ppm) that were effective in reducing the particulate loading caused a decrease in particle size over the entire range of measurement (0.5 micron to 14 micron). Figure 16 indicates that these additives reduced the equivalent aerodynamic mass mean diameter from approximately 2 microns (with no additive) to less than 0.5 micron. However, these additives reduced the total amount of respirable particulate emission (fine particles smaller than 3 microns).

Effect of Additives on Sulfates, Nitrates, and Trace Metals

Particulate samples were analyzed for sulfates, nitrates, and trace metals for about 30 runs with and without additives. The sulfate and nitrate analyses indicate that there was no significant difference between the sulfate and nitrate levels found in the particulate catch for additive and nonadditive runs.

Sulfates. If additive action can be attributed to a catalytic reaction, it may be hypothesized that additives effective in reducing carbon particulate also may increase sulfate level. It was conjectured that these additives not only promoted the catalytic reaction of carbon burnout, but also promoted the reaction of sulfur dioxide to sulfur trioxide and, consequently, to a sulfate. However, the data did not confirm this hypothesis as indicated in Figure 17, a plot of carbon content as a function of sulfate content from the analysis of the filter catch for evaluation runs with and without additives. Examination of the data utilizing the Medial Test (21) indicates no significant relation between carbon and sulfate levels. In addition, Figure 17 indicates that the additives had no significant effect on sulfate levels but had a significant effect in reducing carbon levels.

Nitrates. Analysis of the particulate filter catch indicates that less than 0.1 percent of the filter catch was measured as a nitrate. Additives had no measurable effect on this level.

Trace Metals. Trace metal content of the particulate samples were determined by a semiquantitative emission spectrographic analysis. Because the trace metal analysis was semiquantitative and the level of metal addition

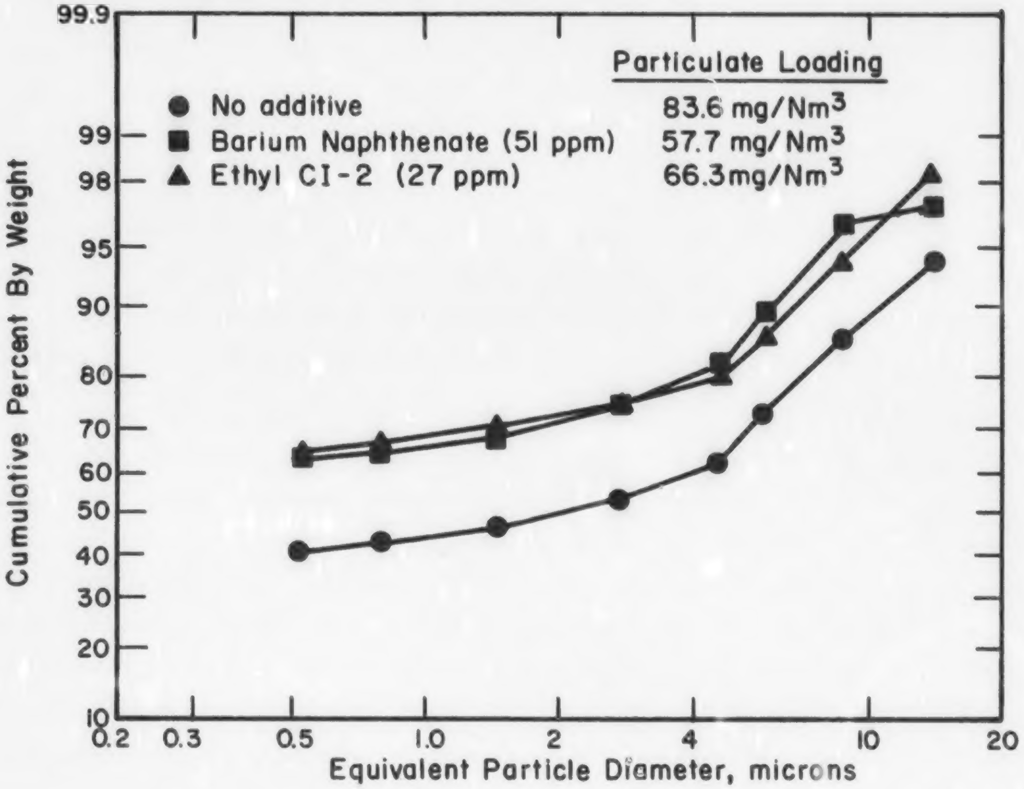

FIGURE 16. PARTICLE-SIZE DISTRIBUTION FOR RUNS
WITH AND WITHOUT ADDITIVES

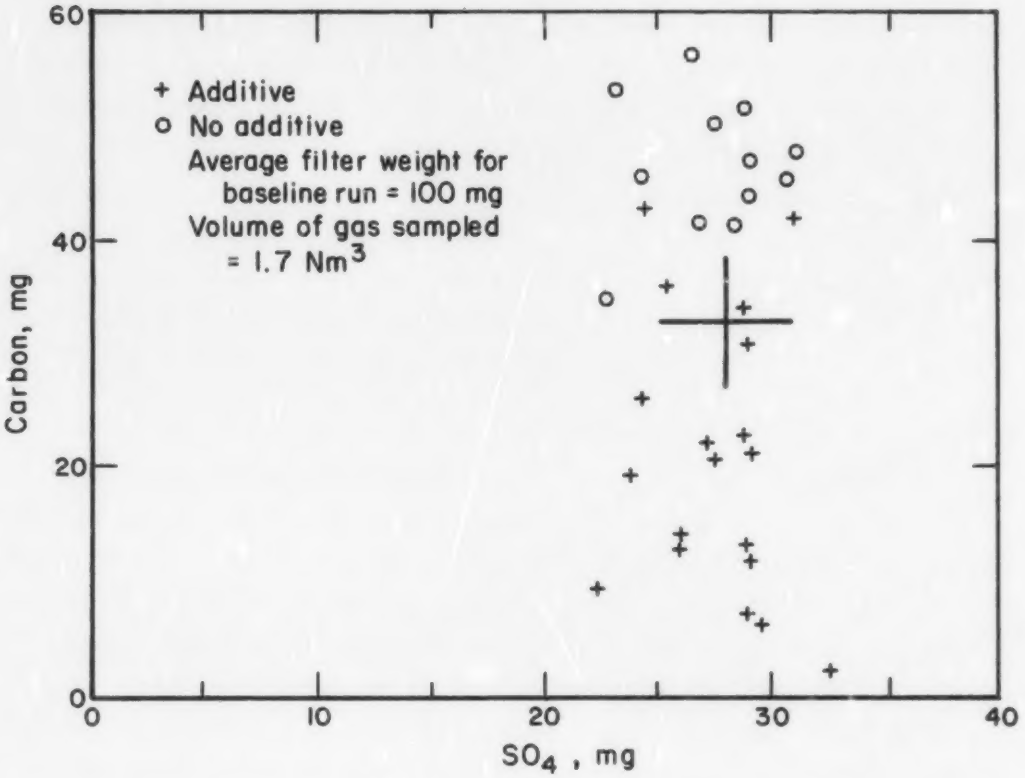

FIGURE 17. MEDIAL TEST APPLIED TO PLOT OF CARBON CONTENT OF FILTER AS A FUNCTION OF SULFATE LEVEL OF FILTER

into the oil was about 10 percent of the inerts contained in the oil, a mass balance for a given metal could not be conducted. However, the analyses indicated the expected result that the use of metal-containing additive increased the corresponding metal content of the particulate catch.

Effect of Additives on Gaseous Emissions

Gaseous emission (NO, SO_2, CO, and HC) were measured over a range of air/fuel ratios for each additive run and the corresponding baseline run. Additives were observed not to significantly effect the emission levels of nitrogen oxide, sulfur dioxide, carbon monoxide, and gaseous hydrocarbons. Although it appears possible that additives may be effective in reducing carbon monoxide and gaseous hydrocarbon emission levels, these levels ($CO < 15$ ppm and $HC < 10$ ppm) were almost negligible for the baseline condition, so that there was no potential for additives to be effective in reducing these emissions. Nitrogen oxide and sulfur dioxide emission levels were measured as approximately 250 ppm and 950 ppm, respectively, firing the 2 percent sulfur residual oil at 12.8 percent CO_2 with and without an additive.

Effect of Additives on Boiler Efficiency

Incremental gains in efficiency by utilization of certain additives can be achieved through a reduction in excess air levels and/or a reduction in fouling of heat transfer surfaces. These incremental gains can be assessed by comparison of (1) the excess-air levels of boiler operation at a constant smoke or particulate level, and (2) the rate of fouling of heat-transfer surfaces (the time-rate of change of stack-gas temperature) with and without the additives. The incremental gains observed in this experimental program were based upon relative differences (in excess air and stack temperature) rather than measurement of absolute overall efficiency as determined by the ASME Power Test Codes.

The incremental change in boiler efficiency for each additive run is not given, as this determination is not a direct measurement; however, the particulate loading ratios, determined by a direct measurement technique, listed in Tables 5 and 6 give an indication of the potential for efficiency improvement. Those additives (certain formulations contain alkaline-earth and/or transition metals) that are the most effective in reducing particulate levels were also observed to be the most effective in increasing boiler efficiency.

Two types of evaluation runs, (1) short term, and (2) long term, were used to determine the incremental gain in efficiency by additive utilization for steady-state operation. The short-term runs were about two hours in duration, in which the effect of additive to reduce excess air levels for a given smoke or a particulate level was determined. The effect of the additive on heating-surface fouling was determined in the long-term runs which were up to 80 hours in duration.

Short-Term Runs. The effect of an additive on boiler efficiency can be estimated from the smoke characteristic curves that are generated during each evaluation run. Figure 13 shows that the use of certain types of additives can shift this characteristic smoke curve to the right (to lower excess air levels for the same smoke number). As indicated for a Bacharach smoke number of 4, the use of cobalt naphthenate (Run 31) and barium naphthenate (Run 26) can decrease the excess air levels from the baseline condition of 22 percent to 10 and 5 percent, respectively. This decrease in excess air corresponds to an incremental gain in efficiency of approximately 0.9 percent for Run 31 and approximately 1.3 percent for Run 26, assuming a stack-gas temperature of 450 F (230 C). (A decrease in excess air level also causes a slight decrease in stack-gas temperature, resulting in a slight additional increase in efficiency. This factor was not included in estimating the efficiency gain.)

Long-Term Runs. Figure 18 is a plot of the stack-gas temperature as a function of time for the five long-term runs with the 2 percent sulfur residual oil. The two dashed curves (Run 93 and 94) denote runs conducted firing the second load of this oil. The boiler operating conditions for these runs are sumarized in Table 5. Barium naphthenate was used at two boiler operating conditions; one condition (Run 92) at the same excess air level as the baseline run and the other condition (Run 91) at approximately the same smoke density and the same particulate loading as the baseline run.

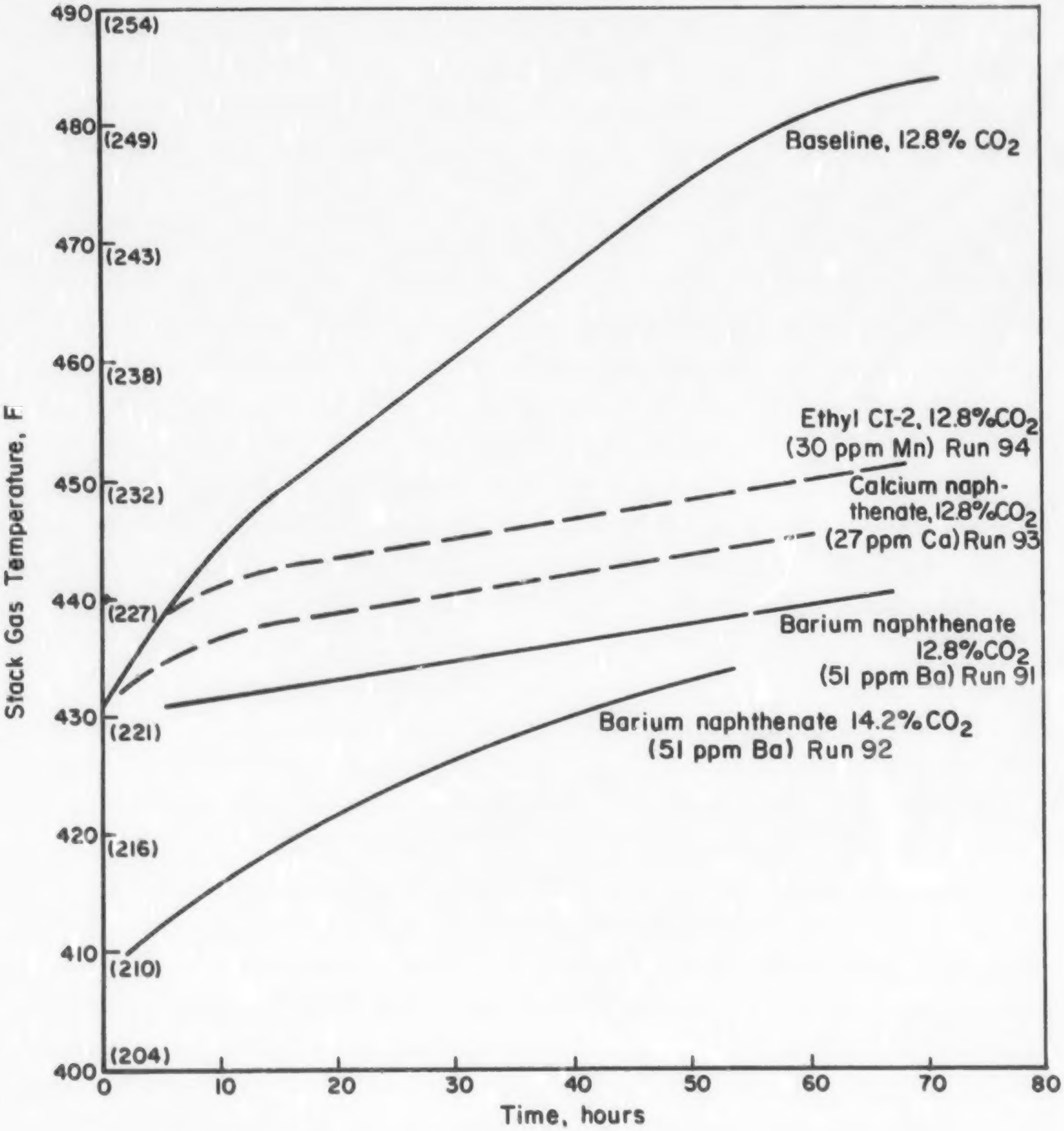

FIGURE 18. STACK-GAS TEMPERATURE AS A FUNCTION OF TIME FIRING TWO-PERCENT SULFUR OIL AT 80 LB/HR

The objective of these long-term runs was to obtain a measure of the fouling of the boiler heat-transfer surfaces with and without additives. From comparison of the stack-gas temperature profiles of the additive Runs 92, 93, and 94 with that of the baseline, it is apparent that these additives are effective in reducing fouling of the heat transfer surfaces during the first 60 hours. It is difficult to extrapolate these curves to obtain a measure of the fouling over an extended period of time, particularly in the case of the baseline run where an apparent decrease in slope occurred after 50 to 60 hours of operation. However, if it is assumed that the time-rate-of-change of the stack-gas temperature (the slope of the curves) is approximately the same after 60 hours, it can then be determined that an incremental increase in efficiency of about 1 percent can be achieved by a reduction in fouling (lower stack temperature) by the use of additives.

In additive Run 91, the excess-air level was reduced to generate the same particulate and smoke levels as the baseline run. As previously discussed, a reduction in excess-air level increases efficiency by reducing the mass of the flue gas and lowering stack-gas temperature. This decrease in stack temperature is in addition to that realized by a reduction in fouling. Although the particulate loadings of Run 91 and the baseline are approximately equal, it is apparent from the stack-gas temperature profiles of these runs that the rates of fouling for the additive run is lower than for the baseline runs. This difference may be due to a difference in the character, and possibly the size, of the particulate generated with and without the additive. The combination of the reduction in fouling and the reduction in excess-air level accounts for an overall incremental gain in efficiency of about 2 percent over that of the baseline run. This incremental gain in efficiency of 2 percent was the maximum gain achieved (for the 50-bhp boiler) for the most effective additive, and would be less for the other additives.

The gain in efficiency of about 2 percent achieved in the laboratory boiler does not imply that the same incremental gain can be realized under all field conditions. Additionally, the maximum gain in any boiler would only be achieved with appropriate burner adjustment to allow operation at lower excess air.

SECTION 9

ECONOMICS OF ADDITIVE UTILIZATION

The economics of additive utilization depend upon a number of factors, some of which are definitive such as the cost of the fuel and the additive; others are less definitive, such as the potential for increased boiler efficiency achieved by using additives or the equivalent cost of alternative emission controls. The following discussion provides some guidelines which can be useful in assessing the economics of additive usage for a given boiler installation. To assess efficiency aspects on a national basis would require engineering data on fuel consumption, excess air levels, stack-gas temperatures, smoke density and carbon particulate levels in a variety of typical and well-tuned and maintained boiler systems.

Additive Cost

Table 10 gives the cost of treating 10,000 gallons (37.8 m^3) of fuel, based upon a dosage of 27 ppm metal per gallon of fuel, for the pure and proprietary compounds that were found effective in reducing smoke and carbon particulate (and thus increase efficiency). It should be noted that dosages of greater than 27 ppm metal per gallon of fuel would be required for some of the proprietary additives to be effective in reducing carbon particulate and smoke (and thus increase efficiency). Clearly, the most cost-effective additives were the pure compounds such as calcium naphthenate at a treatment of $18/10,000 gallons, while the treatment cost of the least expensive proprietary additive was $35/10,000 gallons. Use of many of the proprietary additives would be considerably higher than $35/10,000 gal. In addition to the cost of the additive, other costs associated with the handling of the additive must also be considered to determine the actual fuel savings from additive utilization.

TABLE 10. COST OF TREATING 10,000 GALLONS OF FUEL OIL BASED UPON DOSAGE OF 27 PPM METAL/GALLON OF FUEL OIL[(a)]

Additive	Cost of Treatment ($/10,000 gal)
Calcium naphthenate	18
Barium naphthenate	20
Cobalt naphthenate	70
Iron naphthenate	22
Barium ethyl hexoate	60
Iron pentacarbonyl	120
MC-7 soluble (Apollo chemical)	35
Improsoot (commercial chemical)	200
Formula LSD (commercial chemical)	230
Rolfite 404 (Andrew Rolfe chemical)	200
Watcon 130 (industrial chemical)	270
Ferrocene (arapahoe)	50

(a) Cost figures were based upon drum quantities or bulk lots, f.o.b., the point of supply as of October 1, 1975.

Fuel Savings

In addition to the costs associated with the additive, the fuel savings realized from additive use are dependent upon the fuel cost and efficiency as indicated in Figure 19. Thus, for the least expensive pure compounds, incremental gains in efficiency of 0.6 percent would have to be realized to economically justify additive utilization, while they would have to be at least 1.5 percent for the least expensive proprietary. From Figure 19 it can be observed that as the price of fuel increases (assuming the cost of the additive does not), the incremental gain in efficiency need not be as great to justify the use of the additives.

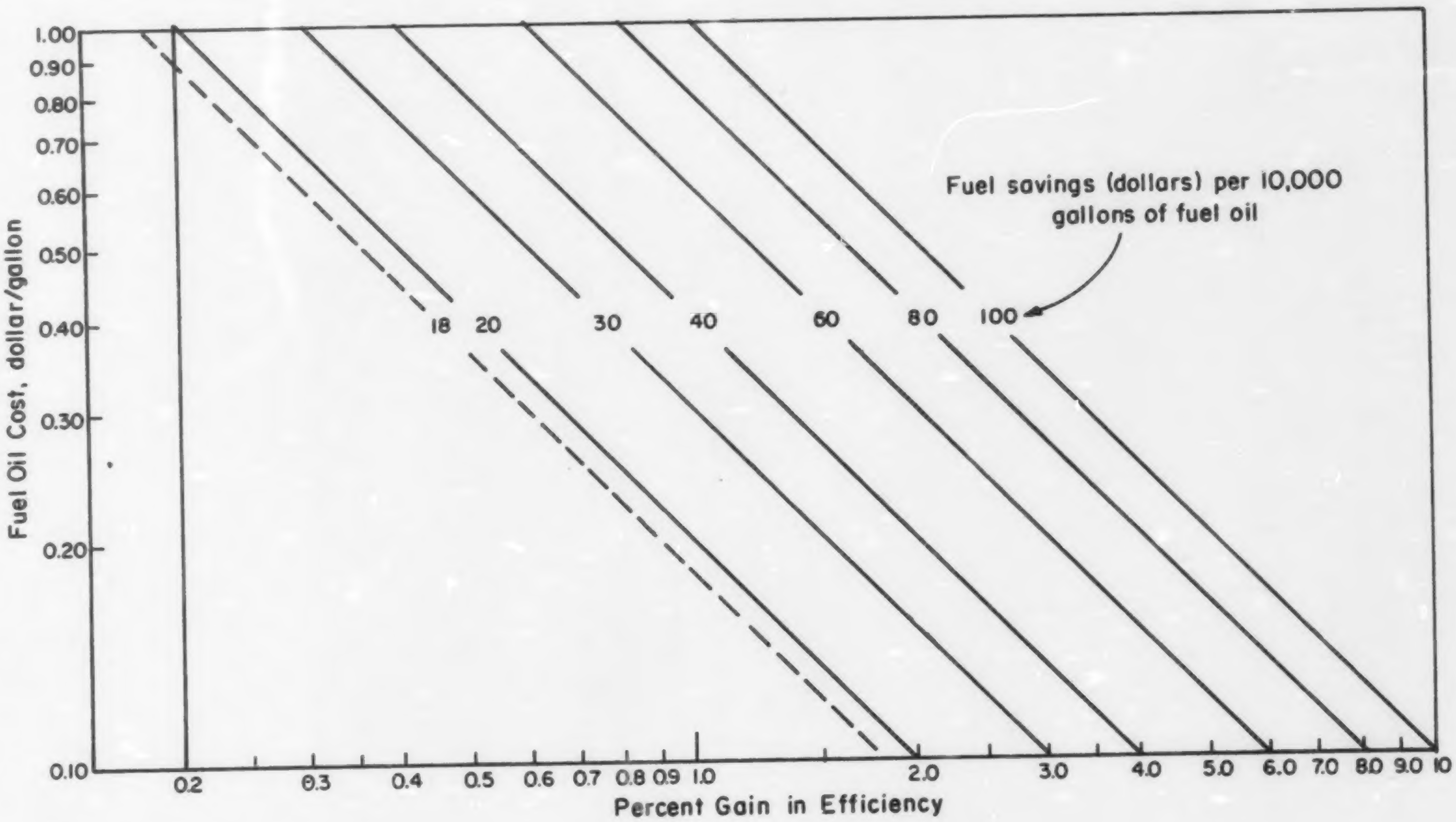

FIGURE 19. FUEL SAVINGS ACHIEVED BY THE UTILIZATION OF ADDITIVES

In terms of generating steam, the use of least expensive pure compounds in an appropriately adjusted boiler to achieve a 2 percent incremental gain in efficiency results in a fuel savings of $50 per million pounds of steam generated. This calculation was based on a fuel cost of $0.30 gallon, a boiler efficiency of approximately 80 percent, and additive treatment cost of $20/10,000 gallons. For a 50-hp boiler and using an annual load factor of 0.25 for this type of boiler (22) a net savings of about $150/yr would be achieved by the use of pure compounds, not considering additional equipment costs. Including the capital costs (pump, mixing section, etc.) and maintenance of an additive handling system, this fuel saving would be reduced; it is questionable whether the use of even the least expensive pure compounds can be economically justified in this size of equipment. However, the increase in boiler efficiency does extend allotment or supply of fuel oil which may be a more important consideration under some circumstances than the fuel cost savings.

SECTION 10

POSSIBLE MECHANISMS BY WHICH ADDITIVES AFFECT PARTICULATE EMISSIONS

To explain the difference in performance by the various metals which achieved some reduction in the particulate emissions, it is necessary to hypothesize as to the mechanism by which they act. The transition metals, iron, manganese, and cobalt, are known to be oxidation catalysts in a variety of chemical systems. Consequently, their activity could be attributed to catalytic enhancement of the carbon burnout in the fly ash. Differences among these metals could result from the degree of catalysis displayed by the particular metal. However, in these experiments, no statistically significant difference was found between the performance of these three metals.

The alkaline-earth metals, barium and calcium, are not noted for catalytic activity, so the mechanism by which they reduce particulates is likely very different from that of the transition metals. It has been suggested by Friswell (23) that alkaline-earth metals may function by promoting the dissociation of water to H atoms and OH radicals, a process occurring only at high temperature. The OH radicals are involved in the combustion of carbon:

$$C + OH \rightarrow CO + H$$

$$CO + OH \rightarrow CO_2 + H$$

The H atoms, in turn, react with oxygen in the combustion air to form additional OH radicals and O atoms, namely, $O_2 + OH \rightarrow H + O$.

For differences between various compounds of the same metal, the bond strength between the metal and the remainder of the molecule may be the controlling factor. This aspect was explored most completely for barium. The number of available materials was limited by the necessity that they be soluble in the oil. In this investigation, the naphthenate, hexoate, and the sulfonate were used, all of which are barium salts of organic acids. Although some differences in performance of these barium derivatives can be noted from the data presented in Tables 5 and 6, additional data are needed to make a statistically valid evaluation. In the cases of iron and manganese, the situation is similar, although the compounds used for this study cannot be as readily compared. These mechanistic considerations can be used to explain differences, but the possibility should not be eliminated that other properties, such as volatility of the additive and the nature of the oil, may influence the effectiveness of the additive in reducing particulate emissions.

The possible mechanisms of additive actions are discussed in greater detail in the state-of-the-art report (3); excerpts of that summary are reproduced in Appendix A of this report.

SECTION 11

PERSPECTIVE ON FUEL ADDITIVES

In this study, additives containing certain metals used at concentrations of approximately 20 ppm to 50 ppm of metal in the fuel oil were found effective in reducing carbon particulate emissions and, therefore, total particulate emissions.Although the scope of this program considered other pollutants besides carbonaceous particulate, additives were not found effective in reducing other pollutants.

The results of this study, for the most part, have confirmed the observations of other researchers and have extended the range of investigation of proprietary additives and pure compounds to include well-controlled tests in commercial-size combustion equipment firing residual fuel oil. It should be re-emphasized that the mechanisms involved in additive action are not fully understood and there is evidence to indicate that additives effective in one system firing one type of fuel may not be equally effective in another system or when firing a different fuel.

Although the mechanistic actions were not directly investigated experimentally, theoretical considerations and limited data suggest that a better understanding of these mechanisms can ultimately lead to additive utilization criteria for many types of combustion systems (3). Mechanisms of nucleation and catalysis should be considered further in light of the interrelation of the combustion system, fuel properties, and additive type and concentration.

POSSIBLE LIMITATIONS TO THE USE OF ADDITIVES

Before any general or widespread use of fuel-oil additives can be recommended, a perspective should be developed for each type of boiler installation, to include these additional considerations:

- Combined emission impact, including effects of the additive on various pollutants

- Possible toxic effects of trace pollutant emissions resulting from materials introduced with the additives

- Effects of equipment characteristics on fuel additive effectiveness

- Practical considerations of additive use, other than simply the reduction of one or more pollutants

- Comparison of the effectiveness of additives with alternative control means.

Because of the wide variability of boiler/burner designs and operating conditons expected in commercial and industrial use, a field test program would be an essential part of any general assessment of additive effectiveness. However, the incentives for such a program may be low in view of the relatively low benefits gained by additive utilization in comparison with other alternatives.

Additional comments on each of these possible limitations are presented below.

Overall Emission Impact

The overall or net impact of a fuel additive on a number of different pollutants must be considered in combination so that means for solving one pollutant problem do not create another problem by bringing about an increase in another pollutant. For example, some additives may affect reductions in one pollutant but increase the emission of another pollutant.

Toxic Effects

Included in the overall consideration of additive usage is the possibility that materials present in additives may produce pollutants which are toxic. For example, metal-containing additives will result in emissions of the metal or metals, the possible adverse health effects of which must be balanced against the reduced emissions of the target pollutant. In many cases, the potential adverse effects of such emissions are not adequately understood.

The Effect of Equipment Characteristics on Fuel Additive Effectiveness

In the case of fuel impurities (such as sulfur and heavy metals) and the nitrogen oxides, the evidence for additive effectiveness is too uncertain and the possible modes of action too obscure to permit any rational discussion of how their effectiveness may be influenced by equipment characteristics.

In some case of products of incomplete combustion, especially carbon particulates and soot or smoke, there is both experimental evidence of additive effectiveness in continuous combustion systems and reasonable conjecture as to how the additives function. Consequently, for additives effective in reducing smoke and carbon particulate, some consideration of the influence of equipment characteristics, or combustion conditions, is possible. Such influences may explain the varying degrees of effectiveness found for the same or similar additive by different investigators. Following are some examples of equipment characteristics that may influence additive effectiveness.

Effects of Fuel-Air Ratio. It is easy to conceive that fuel-air ratio may affect the performance of additives intended to control emissions of products of incomplete combustion, since, in the extreme case of substoichiometric air, combustion must be incomplete regardless of additive effectiveness. The suggestion that barium functions as a free radical promoter and is thus active in the high-temperature region of active combustion, while the transition metals accelerate the oxidation of solid carbon in the post-flame region, has been proposed as an explanation for an observed difference in the effectiveness of these additives at differing fuel-air ratios. Thus, the effectiveness of barium in suppressing smoke was little affected by the overall fuel-air ratio, while the effectiveness of the transition metal manganese was observed to decline with excess air.

Effects of Time-Temperature Relationships. The belief that the transition metals are active in the postflame region also suggests that their effectiveness may be influenced by the rate of heat extraction from the combustion products. If the combustion space is small and the products cooled rapidly, the catalyzed oxidation of the carbon particles may be quenched and the transition-metal additives would be relatively ineffective. Such rapid postflame cooling would have a lesser effect on the action of barium or, assuming a similar basis of action, the other alkaline earth metals because this type of additive is thought to be active at high temperatures. In contrast, low combustion temperature, such as accompanying two-stage or distributed combustion, might reduce the effectiveness of the alkaline earth metals without greatly affecting the activity of the transition metals.

Effects of Fuel Vaporization and Fuel-Air Mixing. The possibility exists for the fuel additive to be separated from the region where its activity is needed. Thus, an additive retained in a coke or ash particle would be ineffective in reducing smoke emissions. Likewise, smoke formed during the initial burning of the fuel might be little affected by an additive released from the liquid fuel at a latter stage of the combustion process. Separations such as these, or their reverse, will be influenced by the volatility and thermal stability of the additive, the character of the fuel, and the thermal regime characterizing the vaporization zone of the equipment.

At the moment, the above descriptions of possible influences of equipment types on additive effectiveness must be regarded as providing a basis for anticipating such influences rather than being definitive examples. Experimental investigations under controlled conditions will be required to identify the parameters of importance for various equipment and additive types.

Other Practical Considerations

Practical considerations that may limit the feasibility of additives include possible effects on (1) storage stability and handling characteristics of specific fuels, or (2) deposits in burner parts of flue passes. (Storage stability includes such aspects as sediment, gum formation, and especially moisture sensitivity. A review of Class I fuel-handling additives is contained in Appendix B of this report.) Such effects may not be easily predictable without investigation of additives under specific field conditions to be encountered.

Alternative Approaches

Other alternative means of emission control and increasing efficiency may be more effective than the use of additives in many applications. Because particulate emission control and increased efficiency are somewhat competing and maximizing one may reduce the other, alternative concepts to additive use may be more attractive. Both practical effectiveness and cost effectiveness should be considered.

Emission Control--

The most viable approach to control of particulate emissions from oil-fired equipment is to insure proper burner design, correct burner adjustment to obtain good fuel-air mixing, the desired thermal environment and adequate controls to automatically maintain these conditions. Utilization of existing combustion technology generally can reduce emissions resulting from incomplete combustion. Fuel switching from residual oil to distillate oil is an alternative that can reduce emissions but this control strategy must be evaluated in terms of both the availability of distillate oil and the price differential with residual oil.

Another situation where additives may prove useful is in conjunction with combustion modification (such as staged combustion) intended to control nitrogen oxides. If it should develop that such modifications lead to excessive emissions of products of incomplete combustion, especially soot, fuel additives may offer a route to overall emission control. At present, this possibility has not been sufficiently investigated to permit drawing definite conclusions.

Efficiency Gain--

It appears that additive utilization for improved efficiency has its greatest potential in low-pressure boilers with capacities of less than about 30,000 pounds steam per hour. For larger boilers the economics suggest the consideration of heat recovery equipment that can achieve incremental gains in efficiencies of as much as 10 percent, whereas additives may increase efficiencies by only a few percent. Also, in these larger units, boilers are equipped with more sensitive controls than the smaller units and, thereby, are capable of operating with minimal amounts of excess air.

From an economic standpoint, additive utilization at best would be cost effective only if boiler efficiency can be increased by at least 1 percent or at 500 F, an incremental reduction in excess air of about 10 percent. Accordingly, assuming 15 percent excess air as a minimum level for satisfactory boiler operation, the potential exists for additive utilization to be cost effective for those boilers that cannot be "tuned" and operated for extended periods of time at less than 25 percent excess air. It is likely that additive utilization also would reduce fouling so that the incremental reduction in excess air need not be as great as 10 percent for additives to be cost effective. However, it is difficult to characterize every boiler with only one or two parameters. Thus, before any generalized recommendations regarding additive utilization in a specific boiler can be made, the economic aspects of the boiler installation must be assessed.

In short, the needed perspective must include consideration of the full spectrum of pollutants, emission control alternatives and economic aspects of increased efficiency applicable to each type of boiler installation.

APPENDIX A

EXCERPTS FROM COMBUSTION ADDITIVES FOR POLLUTION CONTROL: STATE-OF-THE-ART REVIEW *

ABSTRACT

Fuel additives have been used, or proposed for use, to serve a variety of functions in combustion systems. This report covers a state-of-the-art review of combustion-type fuel additives as to their potential in reducing air-pollutant emissions for oil and coal firing. The report contains two complementary parts: (1) a review of combustion mechanisms as they relate to additive action in controlling emissions, and (2) a review of experimental investigations of combustion-type fuel additives.

The review of technical literature revealed relatively limited quantitative data from experimental investigations on combustion additives in which conditions are well defined. However, there is evidence for some measure of control of emissions by fuel additives.

The evidence for control by fuel additives of visible smoke and carbon particulate is relatively strong, and the evidence for control of polycyclic organic matter (POM) is somewhat weaker. The evidence for control of NO_x is quite weak. Significant control of SO_2 or total sulfur emissions by fuel additives does not appear to be possible, although emissions of SO_3 can be reduced. Possibilities for the control of emissions of ash, or specific ash constituents by fuel additives, is restricted to enhancing the collectability of ash particles. Little experimental evidence is available for control of hydrocarbons or CO emissions by fuel additives, although theoretical considerations suggest that some degree of control might be possible. Practical considerations and other possible limitations to the use of additives are also reviewed.

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* Reference (4)

OVERVIEW AND CONCLUSIONS

The conclusions reached by this overall review are discussed below by the category of pollutants, followed by general comments on the use of fuel additives; then, recommendations are presented relating to further R&D needed to fill gaps in information. Although a number of possibilities for advancing the state-of-the-art are suggested, with few exceptions, the probability of a successful and practically useful outcome for emission control is relatively low, compared to opportunities for improvements by good combustion design and practice.

The following overview summarizes principal conclusions on combustion-type fuel additive effects as related to:

1. Products of incomplete combustion
2. Emissions resulting from fuel impurities
3. Emissions of nitrogen oxides
4. Boiler efficiency

ADDITIVE EFFECTS ON PRODUCTS OF INCOMPLETE COMBUSTION

Products of incomplete combustion include CO, hydrocarbon, POM, smoke or soot, and coke particles. This class of pollutants offers perhaps the most fertile field for additive application. Recorded research is limited to "particulates" (i.e., smoke or soot and coke particles, and POM), although one might expect additives affecting any of the products of incomplete combustion would have detectable effects on the others. Obviously, the ash portion of the particulate emission (or fly ash) cannot be reduced by an additive; however, the combustible or carbon portion can be reduced.

Effects on Combustible Particulates

The greatest effort in fuel additive studies has been devoted to particulate and smoke emissions. For minimizing particulate formation in fuel-oil combustion processes, experimental evidence shows that the most effective agents are compounds of some transition metals (manganese, iron, nickel, and cobalt) and some alkaline-earth metals (barium and calcium).

Organometallic derivatives of these metals have given the best results. The organic portion of the molecule provides the needed solubility in the oil, while also influencing the stability and volatility of the additive molecule.

It is generally proposed that the transition metals catalyze the oxidation of soot in the hot combustion gases. Of the alkaline-earth metals, barium has been suggested to act as a catalyst for the decomposition of hydrogen and water, promoting the destruction of soot by the free radicals thus generated.

No research clearly pertaining to coke-particle emissions was found. While it may reasonably be assumed that the same type of additives effective in reducing smoke or soot emissions will be effective in reducing coke particle emissions, the optimum additive volatility or thermal stability may differ. A possibility exists for the application of selected cracking catalysts to inhibit coke formation from heavy oils.

Finally, questions concerning electrical effects in smoke formation and their relation to the effectiveness of some types of additives have not been resolved. Systematic research with additives selected or designed to produce specific flame ionization levels would be needed to explore this point.

Effects on Polycyclic Organic Matter (POM)

Polycyclic organic matter (POM) comprises a class of potentially hazardous pollutants generally resulting from incomplete combustion (13). This class includes (1) polynuclear aromatic hydrocarbons, commonly identified in the literature as PNA or PAH, and (2) nitrogen-containing heterocyclic compounds.

Only a few investigations have reported the effects of additives on POM emissions, and much of this research has been directed toward diesel engines rather than boiler applications. Thus, the reported effects of such additives as nitroparaffin, nitrate esters, organic peroxides, etc., may have limited meaning in boiler combustion. Also, it should be recognized that most of the investigations reporting on POM were published 5 or 10 years ago; the techniques of collecting and analyzing POM have advanced considerably during that time and are still being developed.

Although the physical state of POM and soot are different, their probable common ancestry and chemical reactivity suggest that an additive effective for one would be at least somewhat effective for the other. This conjecture is generally supported by the experimental evidence, but with one interesting exception: an "oil-soluble barium compound", moderately effective in reducing diesel smoke, was reported as having no effect on POM. If, in fact, barium functions as a free-radical promoter, one would expect it to be particularly effective in reducing POM as compared to the postflame oxidation catalysts, such as the transition metals are believed to be. However, if one accepts the conjecture that an oxidation catalyst-type additive that is effective in reducing soot would also be effective in reducing POM, there still is no reason to assume that the optimum additive stability and volatility would be the same for both pollutants.

While an additive that reduces particulate may affect some reduction in POM emissions, there is a need for additive investigations specifically directed to POM control.

Effects on Carbon Monoxide and Hydrocarbons

CO and hydrocarbons are significant pollutants, but their emission levels are usually relatively low from continuous combustion systems like boilers; consequently, few investigations have been reported on the effects of additives on these pollutants from boilers. Generally, the oxidation-catalysts effective in reducing soot or, especially POM, might be expected to have some effect on CO and hydrocarbon emissions. In view of the relative unimportance of these emissions from boilers, investigation of this aspect does not appear to be justified.

ADDITIVE EFFECTS ON EMISSIONS RESULTING FROM FUEL IMPURITIES

The fuel impurities considered here are sulfur and ash. These impurities are considered pollutants regardless of the form in which they are emitted.

Effects on Sulfur Compounds

Mechanistically, no fuel additive can be expected to have a direct effect on the emission of sulfur present in the fuel. Most of the sulfur in the fuel leaves the system as SO_2 (assuming that the combustion is not unusually fuel rich). Typically, only 1 to 3 percent of the sulfur leaves the system as SO_3, depending on combustion conditions. In addition, emissions can include particulate sulfates. (It may be noted that some additives may change the chemical or physical form of the sulfur emissions to one that is not detected by the sampling and analytical techniques commonly used to determine SO_2 or SO_3 emissions.)

Various fuel additives, mostly basic in character, have been used to scavenge SO_3 or, used in much larger amounts in downstream addition, to scavenge SO_2. (This reaction with SO_2 is typically incomplete, and the additive must be used in quantities substantially greater than the stoichiometric amount to achieve high reductions.) It is possible that an additive could be found that would promote the reaction of SO_2 with basic materials; the reported ability of sodium chloride to enhance the absorption of sulfur oxides by the limestone in fluidized-bed coal combustors suggests that such effects exist. However, the large quantity of basic material required, even if used stoichiometrically, still may limit any practical application in ordinary combustion systems.

Effects on Ash

Additives may change the physical properties of ash, but no additive can be expected to reduce the combustion generation of ash constituents contained in the fuel. However, ash collectability may be influenced. SO_3 and other conditioners are sometimes added in the postcombustion zone to reduce the resistivity of fly ash, and thus promote its collection in electrostatic precipitators. There may also be an opportunity of accomplishing this conditioning through the use of compounds (other than sulfur) added to the fuel.

ADDITIVE EFFECTS ON NITROGEN OXIDES

Nitrogen oxide emissions are attributed to two sources: thermal fixation of nitrogen and the oxidation of organically bound-nitrogen compounds in the fuel. The reported examples of additives causing significant (though not major) reductions in NO_x emissions seem more puzzling than illuminating. The mechanisms by which the observed effects could have been produced are obscure.

Effects on Thermal-Fixation Processes

The importance of O- and N-atom levels in the mechanism for the fixation of nitrogen suggests that additives which might reduce, principally, the concentration of O-atoms could be effective in reducing NO_x. In practice, additives have not been especially effective in this regard. One of the problems is that hypothetical additives which might reduce the O-atom level by promoting atom recombination reactions, or by retarding the combustion reactions leading to O-atom formation, could be too detrimental to the overall combustion process.

Effects on Fuel-Nitrogen Conversion

NO_x is formed more readily from chemically bound-nitrogen species than from the fixation process. To reduce NO_x from fuel-N species requires that the decomposition of the fuel-N be diverted to N_2 or N_2O, rather than active CN or NH species. No additives have been found which accomplish this. Interestingly, however, there is evidence that NH species can limit, and perhaps reduce, the conversion efficiency of fuel-N compounds to NO.

On the basis of the information available, it is possible that some minor degree of NO_x control may be obtained with fuel additives; the probability of practical success, however, still appears questionable.

ADDITIVE EFFECTS ON BOILER EFFICIENCY

Two routes are open to influence boiler efficiency by fuel or combustion additives: (1) through cleaning or maintaining the cleanliness of heat exchanger surfaces, or (2) by controlling pollutants, particularly visible smoke, thus permitting operation at reduced excess air levels. Additives intended to remove or modify soot and other surface deposits have a significant history but are outside the scope of this report. However, additives which suppress smoke (soot) and other carbon particulate may both reduce the rate of fouling of the heat exchange surface and permit operation at lower excess air levels. The possible efficiency gain depends on the smoke-limited excess-air level of the specific burner-boiler combination, its normal rate of fouling, and the frequency of cleaning. Efficiency gains of a few percent may be possible in small boilers which are reasonably maintained and adjusted. In larger boilers, with well-designed fuel-air mixing, equipped with soot blowers and possibly heat-recovery equipment, and subject to skilled maintenance and adjustment, additives offer little promise of efficiency gains.

APPENDIX B

APPRAISAL OF FUEL-HANDLING ADDITIVES*

SUMMARY AND CONCLUSIONS

Additives which fulfill their function prior to the combustion of a fuel oil (Class I additives) are discussed in this appendix. The efficiency of boiler operation sometimes may be enhanced by these fuel-handling additives, because they prevent formation of materials that may clog burner components and possibly reduce efficiency by impairing burner performance.

Fuel-handling additives have been developed to be effective in performing functions as

- Oxidation inhibitors
- Corrosion inhibitors
- Dispersants
- Pour-point depressants
- Metal deactivators
- Antistatic additives
- Biocides.

Additives performing the first three functions are routinely added by most U.S. refineries to No. 2 distillate heating oils as part of the normal "additive package" because nozzle ports for oil burners used in residential and commercial combustion equipment are especially sensitive to clogging. Fuel-handling equipment systems and atomizers designed for heavier fuels are more tolerant to deposits, and these additives are less frequently added by the refiner as a normal procedure. Additives serving the other functions are added as dictated by the nature of the fuel or circumstances of use.

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* Study was conducted as part of the FEA-supported portion of the program.

Inhibiting oxidation of the fuel oil is the most important of the functions of fuel-handling additives. Oxidation results in sludge formation, which causes clogging problems, particularly with distillate oils. Effective antioxidant additives based on amines and phenols have been produced in the past and new types are being developed as fuels with different properties appear on the market. In spite of the antioxidants, some sludge still forms; thus, dispersant additives are used to put the sludge into collodial suspension. The most effective dispersants are metal salts of sulfonic acids and phenols. For many years, ashless additives based on amines have been used and recently amine derivatives of organic phosphates have been developed.

Water in fuel oils will separate and corrode the tanks and lines, so corrosion inhibitors are required. The most successful additives of this type have been high-molecular-weight carboxylic, sulfonic, or phosphoric acids and their neutralization products with organic bases. These compounds displace the water from contact with the metal. Water-soluble inhibitors such as sodium nitrite are often used in residential applications.

To maintain fuel flow, particularly in cold weather, pourpoint depressants are used. These materials are semiresinous polymers of high molecular weight which modify the crystals of waxy substances in the oils. Naphthalene-wax and phenol-wax condensation products have been used for this purpose, but ethylene-vinyl acetate copolymers are in greatest use as pourpoint depressants.

Other types of fuel-handling additives which are used include (1) metal deactivators, which are needed where small amounts of transition metals in the oil catalyze its oxidation, (2) antistatic additives, which prevent the accumulation of electrical charges that can cause fires and explosions, and (3) biocides, which inhibit microbiological deterioration of the oil.

The need for additives to perform the above functions varies with the nature of the application and the optimum choice of additives varies with the nature of the base fuel, its compatability with other fuels, the conditions of its storage, handling, and use. In view of the many variables involved and the lack of "universal additives" that can assure good overall fuel-handling performance on a cost-effective basis with all fuels, the recommendation of the oil refiner should be followed for a particular installation. Many refiners maintain a marketing/technical service staff to evaluate special needs encountered in the field and to make such recommendations. In most cases, an effective "additive package" will already be supplied with the fuel. This treatment, when combined with proper storage tank maintenance, will control most fuel oil problems.

Efficient operation of oil-burning equipment thus can be maintained over a period of service by the use of fuel-handling additives that prevent deterioration of the fuel and clogging of fuel lines, filters, or burner nozzles. However, little information is available in the technical or noncommercial literature that documents quantitative gains in efficiency of equipment operating in the field.

Unlike the case of combustion-type additives, where improper use can increase air pollutant emissions, the misapplication or overdosage of fuel-handling additives is unlikely to result in increased air pollutants. For unusual applications of storage or use, the oil refiner should be consulted. Indiscriminate use of additives could cause incompatability problems that will deteriorate fuel quality.

INTRODUCTION

The objective of this appendix is to review the state-of-the-art of fuel additives which are designed to improve the handling of the fuel oil prior to combustion. These additives contribute to the overall efficiency of the boiler operation by maintaining the handling quality of the fuel prior to introduction into the burner and by affording protection to the burner components.

Additives to fuel oils are needed for several purposes, the most important of which is oxidation inhibition. Both distillate and residual fuel oils are subject to sludge formation as a result of the oxidation of some of the hydrocarbon components of the fuel oil. Sludge can plug oil lines, strainers, and burner nozzles. Additives are also needed to prevent corrosion in the fuel-oil-handling system, to provide detergent and dispersant action, and to emulsify the water that finds its way into the oil. As more low sulfur oils are put into use, additives to depress the pourpoint of the oil have become more important. There are also other functions of additives, such as metal deactivators, antistatic agents and biocides.

The importance of fuel-handling additives for the efficiency of boiler operation has been described in general terms by several authors in recent years (24-26). More detailed discussions of the types of additives and their functions were presented by Guthrie in 1960 (27) and by Lodwick in 1964 (28). Symposia papers on additives have been published by the ASTM (29) and the American Chemical Society (30). Much of the information in these earlier articles was directed to additives for gasoline and kerosines. However, some of the data are appropriate for fuel oils, and this appendix includes the pertinent information from these publications and provides recent data to establish the current status of fuel-handling additives.

OXIDATION INHIBITORS

Fuel oils are essentially mixtures of hydrocarbons, which are subject to oxidation to some extent. Oxidation forms gums which become colloidal, then agglomerate and precipitate. The rate at which the oxidation occurs depends on the molecular structure of the hydrocarbon, which in turn will be affected by the treatment the oil has received. Thus, cracked distilates usually deteriorate faster than straight-run distillates. These oils contain unsaturates which are susceptible to oxidation. Experiments performed in an oxygen atmosphere have shown that sludge formation can occur in as little as 2 to 4 days (31) under such accelerated conditions. The oxidation of the oil resulted in the formation of acids, ketones, aldehydes, and esters from the hydrocarbons.

Scientists are in general agreement that the oxidative deterioration of the fuel oils proceeds by a series of free radical reactions involving the hydrocarbons. Oxygen molecules first react with the hydrocarbon to form the free radicals.

$$RH + O_2 \rightarrow R\cdot + HOO\cdot \quad .$$

The hydrocarbon free radical then reacts further to form a peroxy radical:

$$R\cdot + O_2 \rightarrow ROO\cdot \quad .$$

This in turn reacts with more of the hydrocarbon to generate more R· radicals which continue the chain reaction:

$$ROO\cdot + RH \rightarrow ROOH + R\cdot \quad .$$

The hydroperoxides so formed may add to double bonds in unsaturated molecules to continue the free radical reactions, or they may convert into alcohols, ketones, and acids.

Oxidation inhibitors function by removing the peroxy radicals, thus breaking the chain. The best known and most widely used chain-breaking antioxidants are aromatic amines and alkyl phenols. These function by readily furnishing a hydrogen atom to the peroxy radical:

$$ROO\cdot + InH \rightarrow ROOH + In\cdot \quad .$$

The inhibitor free radical which is formed (In·) then disappears by reacting with another such radical, resulting in an inactive product.

The most commonly used phenol-type oxidation inhibitors are 2,4-dimethyl-6-tert-butyl phenol and 2,6-di-tert-butyl-4-methyl phenol. The first named is a liquid and often is preferred over the second one for this reason, even though the latter is more efficient as an antioxidant. Some typical laboratory results in reducing acid formation and sludge with the second compound are shown in Table 11, where 1.5 percent of the additive completely prevented sludge formation at 175 C in a light oil (32). This dosage is much greater than would be used in practice, and phenol-type additives are normally used at concentrations of a few hundred ppm by weight. Recent work by British investigators claimed that 2-tert-butyl-4-ethyl phenol also is an effective antioxidant (33).

TABLE 11. EFFECT OF PHENOL ADDITIVE[(a)] ON ACID AND SLUDGE FORMATION IN LIGHT OIL

Additive Concentration, Wt Percent	Acid No., mg KOH/g	Sludge, Wt Percent
0.0	1.92	1.64
0.5	1.62	1.24
1.0	1.08	0.44
1.5	0.50	None
2.0	0.21	None

(a) 2,6-di-tert-butyl 4-methyl phenol (Ref. 32).

A number of amines have been employed as antioxidants and the most popular one has been N,N'-di-sec-butyl p-phenylene diamine. This compound can release two hydrogen atoms readily and hence stop two oxidation chains per molecule of the amine. Although the amine-type inhibitor is more effective than the phenols on a weight basis, there is little to choose between them on a cost effectiveness basis. A recent development in the amine-type inhibitors has been the use of amino-guanidine derivatives (34). They have been recommended for use in fuel oils at concentrations from 1 to 10 pounds per 1000 barrels of oil (approximately 3-30 ppm by weight). In oxidation stability tests these derivatives lengthened the induction period by a factor of 2 to 2.4, depending on the derivative used. Amine borates also have been introduced for use as antioxidants (35). These compounds are cyclic borates of polymeric alkanol-amines and were claimed to be effective at a concentration of only 0.001 weight percent (10 ppm).

Compounds containing both phosphorus and sulfur in the form of esters of dithiophosphoric acid have been utilized as fuel oil additives because they function both as antioxidants and corrosion inhibitors. Recently barium and zinc salts of the above esters with cycloalklyphenols have been synthesized (36). It was found that the barium compounds were more effective than the zinc compounds for both purposes. Research into the mechanism by which dithiophosphoric acid esters function has revealed that they react with hydroperoxides formed in the oil to give disulfides and stop the oxidation chain reaction (37). Other multifunctional additives of this type have been made by reacting dithiophosphoric acid with amides of polyisobutenyl carboxylic acid (38). They were demonstrated to function as dispersants for sludge as well as corrosion and oxidation inhibitors.

Another recent development has been the use of glycerol esters containing metal oxides as oxidation inhibitors (39). For this purpose, a mixture containing a glyceryl stearate, a naphthenic oil, a surfactant, and both aluminum and magnesium oxide was recommended for use at a concentration of 0.2 gallon per 1000 gallons of fuel oil (in the order of 200 ppm by weight).

CORROSION INHIBITORS

Fuel oils can become contaminated with rust when water enters the storage or distribution system either by condensation or accidentally. Residual oils in particular are subject to contamination with salt water as a result of being transported in tankers. Because hydrocarbon fuels are essentially nonpolar, they can be easily displaced by water from contact with the metal surface of the storage tanks or transfer lines. As a result a water-sludge blanket will be formed at the metal surface. In the case of residual oils, the potential for corrosion is enhanced by the presence of organic sulfur compounds which are acidic. These acids dissolve in the water-sludge layer and attack the steel containers. The corrosion products in turn increase the sludge formation. The corrosion-inhibiting additives can be used most effectively by adding them to the storage tank. Distillate oils contain even fewer compounds which can reduce corrosion, so these additives are useful in the light fuels as well, particularly to prevent surface roughness in pipelines, which would increase pressure drop.

The most successful materials which have been used as additives against corrosion are high molecular weight carboxylic, sulfonic, or phosphoric acids, salts of these acids, and products of neutralization of the acids with organic bases such as amines. When dissolved in the hydrocarbons, these materials have the property of forming an adsorbed film on the metal in contact with the liquid. This film is hydrophobic and displaces the water from the metal surface. The polar end of the inhibitor molecule becomes attached to the metal surface while the other end of the molecule is dissolved in the fuels. If sufficient inhibitor is present, a compact barrier layer of its molecules on the metal prevents penetration by water. Corrosion is then prevented by this impermeable monomolecular film.

Although amine derivatives of phosphates and sulfonates have been used predominantly as corrosion inhibitors in past years, new formulations continue to appear. Typical materials in use are shown in Table 12. A new approach to napthalene sulfonates has recently been developed in France, in which a long-chain unsaturated hydrocarbon containing 15 to 20 carbon atoms is condensed with the naphthalene before sulfonation (40).

TABLE 12. TYPES OF CORROSION INHIBITORS[a]

Material	Recommended Concentration,[b] lb/1000 barrels oil
Alkyl amino phosphate	5.5 - 20
Ethylene diamine dinonyl naphthalene sulfonate	17 - 20
Octyl phosphate ester + octylamines + octyl alcohols	7 - 20
Dimerized linoleic acid	4 - 16

(a) Ref. 28.

(b) 1 lb/1000 barrels is approximately 3 ppm by weight.

Succinic acid derivatives also are being introduced as corrosion inhibitors. One such additive contains a substituted succinic acid and an aliphatic tertiary amine (41). Another formulation consists of the magnesium salt of a substituted succinic acid (42). Several new anticorrosion agents for fuel oils incorporate amines into the mixture in some fashion. These include amine dicarboxylic acids (43), alkyl aminopropanol (44), a polyalkylene amine mixed with a nitrated oil and a polybasic organic acid (45), and reaction products of amines with phenols and aldehydes (46).

Synergistic mixtures of diamides are formed by condensing dicarboxylic acids with diamines. Steel samples were exposed to distillate oils with and without the additives, at a temperature of 100 F. Sixty-five percent of the steel surface was rusted in 4 hours without the additive, while in the presence of the diamides, at concentrations of 1 and 2 pounds per 1000 barrels (approximately 3-6 ppm), only 20 percent of the steel was rusted. However, the best additives will keep rusting below 5 percent in such circumstances.

Magnesium compounds also have been developed for anticorrosion purposes. One such formulation includes magnesium hydroxy carboxylic acid in an organic solvent (48). Another consists of magnesium hydroxide and sodium stearate mixed in a water suspension, then dried and milled to a particle size of 0.05 micrometer. This additive is designed to be introduced into the oil as a powder, and good dispersability is claimed (49).

DISPERSANTS

Even though antioxidants are added to fuel oils, some sludge may still be formed, particularly if the storage period is lengthy. Carryover of sludge particles can plug fuel filters and severely reduce oil preheater efficiency. In distillates, dispersants combat filter plugging caused by bacteria and dirt as well. Particularly in the case of residual oils, efficient combustion requires optimum atomization, which in turn depends on a uniform supply of oil having a controlled viscosity. The presence of sludge adversely affects these parameters, and can also foul or plug burner tips, thereby making it difficult to maintain stable burner conditions. All of these problems can be alleviated by a sludge-dispersant additive, used at concentrations up to 150 ppm by weight in distillates and up to 500 ppm in residual oils. A dispersant additive should be used cautiously if sludge has accumulated in the storage tank. Otherwise the surfactant property of the additive may bring enough of the sludge into suspension to cause clogging problems.

A dispersant functions by absorbing on the surfaces of materials which are insoluble in the oil and converting them into stable colloidal suspensions. Various petroleum and metal sulfonates, metal phenolates, dialkyl dithiophosphates of metals, and metal phenol sulfides possess these dispersing properties and have been used in the past years as dispersant additives. Electron microscope examination of the action of calcium sulfonate and barium dialkyl dithiophosphate additives on asphaltene sludges has shown that particles originally 2 to 4 micrometers in diameter are reduced to less than 0.1 micrometer by the dispersing action (50). In general, barium salts are better dispersants than calcium salts of the same organic compound. Many factors have been shown to be important in determining the effectiveness of a dispersant. Thus, for example, the activity of a sulfonate salt depends on the molecular weight of the sulfonic acid, the solubility of the sulfonate in the oil, the nature of the metal forming the salt, and the catalytic effect of the salt on the oil oxidation (32). The difference in dispersing ability of various metal sulfonates is shown in Table 13, in terms of the length of time required to centrifuge a carbon black suspension out of the treated oil. Although the cobalt and lead derivatives showed a slightly greater dispersant efficiency than barium, the latter is usually used because it is more cost effective.

TABLE 13. COMPARISON OF DISPERSANT EFFECT OF SALTS OF ISOCETYL BENZENE SULFONIC ACID(a)

Oil Treatment	Centrifuging Time, minutes
No additive	70
Calcium salt	90
Barium	105
Strontium	90
Lead	110
Cobalt	140
Copper	80

The development of improved dispersant formulations is required from time to time as new oil sources are found, because different properties are encountered in these oils. For example, the action of a calcium petroleum sulfonate has been shown to be improved by synthesizing a mixture which also contains calcium formate (51). Aluminum sulfonate likewise has been recommended as a dispersant (52). Although barium sulfonate compounds have been used extensively in the past, a barium sulfanilate derivative recently has been recommended for improved performance (53).

Another type of compound which has been developed for sludge dispersancy in recent years is the completely organic structure which has the advantage of being ash free. The monoethanolamine salts of alkyl phosphates are representative of this class of materials (54). Amine salts of phosphate esters derived from polyalcohols also have been synthesized for dispersant purposes (55). An amine phosphate product obtained by reaction with sorbitol dioleate gave a 98 percent flow in a pumping test when added to fuel oil at a concentration of 0.013 g per 100 ml (about 140 ppm). The flow with untreated oil was only 14 percent (56).

Various other mixtures synthesized recently have proved to be successful sludge dispersants. A magnesium derivative of an amine oleate is claimed to combine the ability to disperse sludge with the ability to reduce sulfur dioxide emission, the latter through the action of the magnesium (57). An ethylene oxide-aniline-formaldehyde polymer esterified with oleic acid also has been used (58). Other ashless polymers prepared from maleic, fumaric, vinyl, and methacrylic esters combine the sludge dispersant properties with those of pour-point depressants (59).

POUR-POINT DEPRESSANTS

While pour-point depressants are used in many types of oils, this type of additive is especially useful in residual oils. The residual oils require heated storage tanks and transfer lines to handle them properly. Hence, pour-point depressants can be particularly effective for this type of fuel oil when it is subject to congealing by precipitated wax.

The use of pour-point depressants in distillates is governed by economic considerations, as the additives are an alternate to kerosene dilution or lower distillation endpoint to achieve the desired properties.

Pour-point depressants are made up, in general, of semiresinous high molecular weight polymers. The most important types used in past years have been (1) wax-naphthalene condensation products, (2) phenol-wax condensation products, and (3) methacrylate polymers. These polymers function by modifying the crystals of the waxy substances in the oils, thus reducing formation of immobilizing aggregates (60). Pour-point depressants are effective at concentrations ranging from 0.02 to 0.2 percent by weight (200 to 2000 ppm) depending on the oil and the pour point desired.

There has been a flurry of activity in the development of new formulations for pour-point depressants in recent years. This effort may be the result of greater use of waxy, low-sulfur fuels to meet emission regulations for sulfur oxides. These fuels have higher pour points than were previously encountered. The increased interest may also be the result of oil property variation because new sources are being tapped and new blends are being made. Over 30 patents for new pour-point additives granted in the last few years attest to the significant interest in this field. The types of materials covered by these patents can be classed in seven groups:

1. Ethylene-vinyl ester copolymers, which constitutes the largest number
2. Fatty acid esters of polyhydric alcohols
3. Esters of dicarboxylic acids and polyalcohols
4. Derivatives of amines
5. Mixtures of organic acid chlorides and polymers
6. Derivatives of polymerized olefins
7. Organics mixed with distillate oil fractions.

A list of the materials covered by these patents is presented in Table 14, which includes the pour-point data where available (61-91). The data show that in these cases, a concentration of about 0.1 weight percent (100 ppm) in the fuel oil resulted in a pour-point lowering of 20 to 40 F.

TABLE 14. POUR-POINT DEPRESSANTS DEVELOPED IN RECENT YEARS

Material	Additive Concentration, Wt Percent	Pour Point, °F Without Additive	Pour Point, °F With Additive	Reference
Ethylene-vinyl fatty acid ester copolymer	0.125	80	53	61
" "	ns(a)	70-85	40-45	62
Ethylene-vinyl acetate copolymer + light oil	0.125	79	44	63
Ethylene-vinyl acetate copolymer (high mol. wt.)	0.03	19	1	64
" "	0.1	ns	ns	65
" "	0.1	ns	ns	66
Ethylene-vinyl ester copolymer + recycle oil	ns	ns	ns	67
Ethylene-vinyl ester copolymer + solid hydrocarbon	0.001-1.0	ns	ns	68
Ethylene-vinyl acetate copolymer	0.005-0.05	ns	ns	69
"	ns	ns	ns	70
Ethylene-vinyl ester copolymer	ns	ns	ns	71
"	01-0.125	ns	ns	72
d-Methyl glucoside palmitate	0.1	10	-35	73
Lauryl fumarate polymer	0.1-2	6	-27	74
Sorbitan tristearate	0.05	ns	ns	75
Amylose stearate	0.002-0.2	ns	ns	76
Succinic or maleic anhydride + polyalcohol	0.15	104	70	77
Maleic anhydride + C_{22} alcohol + polymer	0.1	45	25	78
Succinic anhydride + C_{22} alcohol + C_{22} acid	ns	ns	ns	79
N,N-dialkylricinoleamide	0.1	5-10	-35 to -30	80
Fatty diamine + kerosine	1.5	ns	50° lowering	81
C_{21}-alkyl acrylate-vinyl pyridine copolymer	0.04	84	59	82
Methylalkyl amine-epichlorohydrin polymer	ns	ns	ns	83
Allyl phenol polymer-arachidoyl ester	1.0	70	35	84
Allyl chloride-octadecene	0.05-1.0	ns	ns	85

(a) ns = not specified.

(continued)

TABLE 14. (Continued)

Material	Additive Concentration, Wt Percent	Pour Point, °F Without Additive	Pour Point, °F With Additive	Reference
Butadiene-styrene copolymer	ns	-5	-40	86
C_{12}-C_{18} alklyated polystyrene	ns	ns	ns	87
Chlorinated polyethylene with aromatic sidechain	ns	ns	ns	88
Polypropylene	ns	ns	ns	89
Aliphatic alcohols, paraffins, carbonyls, others	ns	ns	ns	90
Middle distillate oil fraction	ns	ns	ns	91

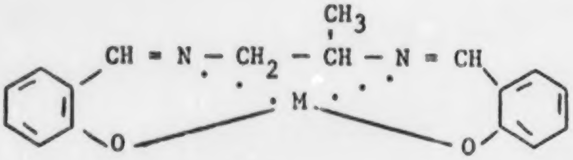
(a) ns = not specified.

MISCELLANEOUS ADDITIVE TYPES

Other types of additives are used for fuel oils to a lesser degree than those previously discussed. The source of the oil and its treatment prior to use will determine whether or not a metal deactivator additive is needed. The conditions of pumping and spark-generating hazards may dictate the need for an antistatic additive. The susceptibility of some oils to microbial growth may require the addition of a biocide. Additives have been developed to fulfill each of these purposes.

Metal Deactivators

The metal content of a fuel oil can catalyze the oxidation of the oil and result in more rapid sludge formation than would otherwise be the case. In addition, mercaptide gels can form on copper and brass parts of the fuel system. Although metals are more concentrated in residual oils than in the original crude, they are tied up in porphyrin-type complexes and are relatively inactive. However, even distillate fuel may contain several parts per million of copper, iron, manganese, zinc, lead, nickel, calcium barium, sodium, potassium, and lithium (92). Of these, the transition metals, copper, iron, manganese, and nickel are the most potent catalysts, and metal deactivators are designed to affect them especially. These metals are powerful hydroperoxide decomposers and act as a catalytic means of providing a constant source of free radicals for oxidation chain initiation. However, by complexing the metal with an organic molecule, it can be prevented from participating in such catalytic activity. Large molecules which can "surround" the metal atom to form a chelate compound are used as deactivators. The compound N,N'-disalicylidene 1,2-propylene diamine is very effective in some cases:



In this formula M represents a bivalent metal which has covalent bonds to the oxygen atoms and coordination bonds with unshared electron pairs on the nitrogen atoms. Copper can be effectively prevented from further reaction by formation of such a compound.

In addition to the diamine shown above, other organic compounds containing nitrogen and oxygen in suitable positions to chelate the metal atom have proven to be useful deactivators. However, formation of the chelate does not always assure deactivation, and some combinations of metal and organic compound actually are activators, because of increased electron transfer capabilities. This effect is illustrated in Table 15 which shows both deactivation and activation by some organic compounds. Copper is completely deactivated by all of them, but only one of these compounds works successfully with manganese. Consequently, it is important to know which of the metals predominate in the oil in order to select the proper additive. In general, copper is the commonest contaminant, probably because copper chloride is sometimes used to convert mercaptans into disulfides during refining. There can also be copper pickup from valves and pumps in the distribution system. Fortunately, copper is relatively easy to deactivate, but nickel and manganese would present problems. The obvious solution would be to use an additive which deactivates all four metals, such as the tetrasalicylidene derivative in Table 15, but such materials are more expensive. Thus, additive cost may be a consideration, although deactivators are used at a concentration of only 5 to 10 ppm by weight.

A recent development in this field is the use of amido triazoles as chelating compounds (93). The simplest of these compounds involves bonding with oxygen and nitrogen as illustrated above. However, some compounds of this type can be made with a sulfur atom in the molecule. The bonding to the metal can then be accomplished via sulfur and nitrogen, thus providing a stronger chelation effect.

TABLE 15. EFFICIENCY OF METAL DEACTIVATORS(a)

Compound	Deactivation (-) or Activation (+), percentage for metal at indicated concentration, ppm			
	Cu 1.0	Fe 0.87	Ni 0.92	Mn 0.86
N,N'-Disalicylidene 1,2-propylene diamine	-100	+43	nd(b)	+103
Salicylaldoxime	-100	0	-100	nd
N-Salicylidene-o-aminophenol	-100	-100	+55	+84
2,2',4'-Trihydroxyazobenzene	-100	-100	+124	+73
N,N',N",N"'-Tetrasalicylidene tetra(aminomethyl) methane	-100	-100	-100	-100

(a) Reference 28.
(b) nd = not determined.

ANTISTATIC ADDITIVES

Explosions and fires caused by static electrical discharges can occur in fuel storage tanks and lines both during storage and handling. Although this problem is most important for aviation fuels, antistatic additives have been developed for use in other distillate fuels. When a fuel oil of low electrical conductivity flows through a pipe, a separation of electrical charges can occur and a static charge is built up in the liquid. This charge separation can lead to high voltages with the possibility of spark discharges which may ignite the fuel vapors. Charge generation is increased by high pumping rates or by contact with equipment having a high surface area such as water separators or fuel filters. However, if the fuel conductivity is increased by an additive, the charge built up in the liquid can leak back to the container wall.

The antistatic additives used in the past have been three-component systems consisting of (1) the chromium salt of an alkylated salicylic acid, (2) calcium di(2-ethylhexyl) sulfo-succinate, and (3) an organic polymer, which functions as the additive stabilizing agent. Such an additive when used at a concentration of about 1 ppm will raise the conductivity of a jet fuel to what is considered a safe level (50 picomho/meter).

A recently developed antistatic additive is the reaction product of an amine with a copolymer of methyl vinyl ether and maleic anhydride (94). The conductivity of a fuel (boiling range 320 to 720) was increased from 9 to 551 picomho/meter by the addition of 5 lb of the product to 1000 barrels of the fuel (about 15 ppm). Another amine-type additive increased the conductivity of a distillate oil by a factor of 100 when 50 ppm of a 1 percent solution in xylene was used (95).

The effectiveness of chromium compounds as additives was demonstrated by the chromium tris (acylanthranilate) class of compounds. When the acyl part of the molecule was from oleic acid, the conductivity of a distillate oil was increased by a factor of 10^4 with the additive at a concentration of 5 g/metric ton (5 ppm) (96). Simple chromium salts of oleic or naphthenic acids also have been recommended as antistatic additives (97). Mixtures of these acids with ferrocene derivatives and cyclopentadienyl manganese tricarbonyl also are claimed to be effective.

Synergistic effects also have been observed in antistatic additives for distillate fuels (98). The antistatic activity of barium and zinc naphthenates and octoates was enhanced by mixing them with another additive composition based on tallow diamine and alkyl phosphates.

BIOCIDES

Although some light oils can be used to control biocidal attack on selected crops, the fuel oils themselves can be subject to attack by bacteria and fungi. These organisms can grow at an oil-water interface in storage tanks in all climates, and it can be particularly serious in tropical climates where both the temperature and the humidity are high. This attack generates materials in the oils which can clog the fuel filters.

Trialkyl benzylammonium salts have been recommended as fungicides for fuel oils (99). Derivatives made with long-chain alkyl groups ranging from C_8 to C_{22} were used. In addition, cetyl pyridinium sulfates also were found effective. Boron compounds are widely used as oil-soluble bactericides. Compounds containing two nitrogen atoms in a five-membered ring structure (pyrazolidones) with three alkyl or aryl sidechains likewise have been developed as additives to inhibit the microbiological contamination of petroleum products (100).

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